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ARTICLE

Effect of direct ultrasound synthesis via a sesquihydrate route on bismuth-promoted vanadyl pyrophosphate catalysts

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Abstract

A series of 1, 3, and 5% Bi-doped vanadium phosphate catalyst catalysts were prepared via sesquihydrate route using direct ultrasound method and were denoted as VPSB1, VPSB3, and VPSB5, respectively. These catalysts were synthesized solely using a direct ultrasound technique and calcined in a *n*-butane/air mixture. This study showed that catalyst synthesis time can be drastically reduced to only 2 hr compared to conventional 32-48 hr. All Bi-doped catalysts exhibited a wellcrystallized (VO)₂P₂O₇ phase. In addition, two V⁵⁺ phases, that is, β -VOPO₄ and α_{II} -VOPO₄, were observed leading to an increase in the average oxidation state of vanadium. All catalysts showed V2p_{3/2} at approx. 517 eV, giving the vanadium oxidation state at approx. 4.3-4.6. Field-emission scanning electron microscopy micrographs showed the secondary structure consisting of thin and small plate-like crystal clusters due to the cavitation effect of ultrasound waves. VPSB5 showed the highest amount of oxygen species removed associated with the V^{5+} and V^{4+} species in temperature-programmed reduction in H₂ analyses. TheX-ray absorption near edge structure (XANES) measurement showed the occurrence of vanadium oxide reductions in hydrogen gas flow, indicating the presence of V^{4+} and V^{5+} species. Higher average valence states of V^{5+} , indicating more V^{5+} phases, were present. The addition of bismuth has increased the activity and selectivity to maleic anhydride.

KEYWORDS

bismuth, butane oxidation, direct ultrasound synthesis, selective oxidation, sesquihydrate, vanadyl pyrophosphate catalyst

1 | INTRODUCTION

The partial oxidation of *n*-butane over the vanadium phosphate catalyst (VPO) is probably the most successful pathway for the production of maleic anhydride.^[1–3] The oxidation of *n*-butane to maleic anhydride using a VPO catalyst is a 14 electron oxidation occurring on the catalyst surface. In this process, eight hydrogen atoms were removed, three oxygen atoms were inserted, and a ring closure occurred.^[4,5] Vanadium pyrophosphate, $(VO)_2P_2O_7$, is known as the active and selective catalyst for the oxidation of *n*-butane to maleic anhydride.

The modification of the VPO catalyst properties by addition of promoters has been growing popularly especially in recent years.^[1–3,6] Beneficial effects such as structural as well as electronic changes or enhancement in the activity and selectivity of the bulk catalyst can be achieved with the addition of promoters. A wide range of cations such as Ce,

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Co, Cd, Ni, Zn, Bi, Cu, Li, V, Zr, Mg, Ti, La, Mo, Nb, B, Fe, and Cr have been reported in patents.^[2,3,5] Among the popular promoters for VPO catalysts, bismuth (Bi) has been intensively studied for the past two decades.^[3,7] Some researchers reported that the addition of bismuth increases the activity and selectivity to maleic anhydride.^[3,6–9] This element promotes the catalytic activity through the generation of surface defects in which the Lewis acid sites are likely associated, thereby enhancing the activation of the alkane.^[6] Past studies on Bi-doped catalysts prepared via the VPD method using the conventional preparation route showed an increment in activity.^[6,10]

It is well known that the catalyst preparation method affects the channel structure, acid site density, oxidation state, and the location of the vanadium species, and these factors were found to affect the catalytic performance of *n*butane conversion.^[11,12] Moreover, the conventional preparation time for the VPO catalyst was reported to be around 32–48 hr,^[3,8,11–14] therefore alternative methods for generating catalysts in a shorter duration are highly desirable.^[11] Some developments in the synthesis technique such as mechanosynthesis, mechanochemical treatment.^[13,15] microwave,^[11,16,17] and hydrothermal^[18] were reported in the past. Recently, the use of ultrasound in chemistry has been discovered to not only enhance the reaction rates but also direct reactions onto different pathways.^[11,12,17,19,20] It is believed that using ultrasound irradiation can enhance the chemical reaction and mass transfer via the process of acoustic cavitation.^[11,21] The ultrasound approach has been used in the preparation of a wide range of chemical materials such as ceramics, alloys, composites, and polymers due to its cavitation effect on chemical processes.^[11,17,20] This cavitation effect caused by the ultrasound waves, that is the sound pressure waves produced under the ultrasound irradiation frequency from ~20 to 100 MHz, could improve the chemical reaction and mass transfer via the physicochemical changes in the medium.^[11,20]

Therefore, in this study, the Bi-doped VPO catalysts were prepared using the vanadyl hydrogen phosphate sesquihydrate precursor (VOHPO₄ \cdot 1.5H₂O) via a direct ultrasound irradiation synthesis process, denoted as the VPSB route. The effects of different percentages of the bismuth promoter on the physicochemical properties, reactivity, and catalytic performances of the VPO catalysts were examined.

2 | RESULTS AND DISCUSSION

2.1 | X-ray diffraction

The X-ray diffraction (XRD) patterns of the undoped and Bi-doped catalysts obtained using direct ultrasound



FIGURE 1 Powder XRD patterns of the undoped and Bi-doped catalysts synthesized using the direct ultrasound method

technique are shown in Figure 1. All the catalysts were found to consist of a mixture of the $(VO)_2P_2O_7$ phase (JCPDS File No. 34-1381) and the V^{5+} phase; i.e., β -VOPO₄ (JCPDS File No. 27-0948) and α_{II} -VOPO₄ (JCPDS File No. 34-1247). The diffractogram of the prepared catalysts showed a similar diffraction pattern comprised of a wellcrystallized $(VO)_2P_2O_7$ phase with the main characteristic peaks appearing at $2\theta = 22.9^{\circ}$, 28.4° , and 29.9° , corresponding to the reflection of (0 2 0), (2 0 4), and (2 2 1) planes, and the additional peaks observed at $2\theta = 25.1^{\circ}$, 27.3°, and 29.3° are attributed to the V^{5+} phase. The peaks of the V^{5+} phases were shown to be more intense as the doping percentage increased, thus indicating that the addition of bismuth promotes the formation of V⁵⁺ phases, which contributes to higher selectivity to maleic anhydride. The existence of the V⁵⁺ phase was also demonstrated in the redox titration and X-ray photoelectron spectroscopy (XPS) analyses later in this article, which showed that Bi-doped catalysts had a higher concentration of V⁵⁺ and average oxidation state compared to the undoped catalysts. The Bidoped catalysts synthesized using the direct ultrasound technique showed similar XRD profile data in comparison to the conventionally prepared Bi-doped catalysts.^[3]

The reflection peaks of Bi-doped VPO catalysts at all three major peaks ($2\theta = 22.9^{\circ}$, 28.4° , and 29.9°) are shown to be less intense with broader width sizes as compared to VPSU. The peak intensities reduced as the amount of doping increased from low to high percentage. The crystallite sizes of the (0 2 0) reflection plane for VPSU, VPSB1, VPSB3, and VPSB5 were calculated as 190.75, 100.14, 79.49, and 125.16 Å respectively, whereas the crystallite sizes of the (2 0 4) reflection plane catalysts produced were 264.03, 70.63, 51.93, and 92.53 Å, respectively (Table 1). Compared to the VPSU, all the Bi-doped catalysts showed an obvious **TABLE 1** The X-ray diffraction data

 of Bi-doped catalysts

Catalyst	Linewidth ^a (0 2 0) (°)	Linewidth^b (2 0 4) (°)	Crystallite size ^c (0 2 0) (Å)	Crystallite size ^c (2 0 4) (Å)
VPSU	0.4200	0.3066	190.75	264.03
VPSB1	0.8000	1.1475	100.14	70.63
VPSB3	1.0080	1.5614	79.49	51.93
VPSB5	0.6400	0.8767	125.16	92.53
VPSRB1 ^d	0.5370	0.6100	149.21	132.79
VPSRB3 ^d	0.4267	0.7080	187.78	114.41
VPSRB5 ^d	0.6767	1.8400	118.4	44.02

^aFWHM of (0 2 0) reflection.

^bFWHM of (2 0 4) reflection.

^cCrystallite thickness obtained by means of Scherrer's formula.

^dConventionally prepared Bi-doped catalysts by Leong et al^[3]

reduction in crystallite sizes. Besides, VPSB1 and VPSB3 prepared using the direct ultrasound technique showed smaller crystallite sizes when compared to the conventionally prepared Bi-doped catalysts (1 and 3%). Whereas VPSB5 produced using the ultrasound method showed higher crystallite sizes compared to the conventionally produced Bi-doped 5% catalysts.^[3] The crystallinity and sharper peaks could be observed in this study with the application of ultrasound. The smaller crystallite sizes allowing a higher surface area may contribute to the improvement in catalytic performances. Furthermore, the catalyst production time was drastically reduced to only 2 hr in the presence of a well-crystallized (VO)₂P₂O₇ phase .^[3,11,14,21,22]

2.2 | X-ray photoelectron spectroscopy

Figure 2 shows a high-resolution XPS spectrum containing the O1s, V2p_{1/2}, and V2p_{3/2} photoelectron peaks for VPSU, VPSB1, VPSB3, and VPSB5. The V2p_{3/2} peak could be separated into two components at 516.9 and 518.0 eV (Figure 2), which can be related to V^{4+} and V^{5+} species, respectively.^[4,17,23–28] The percentages of V^{4+} and V^{5+} species present were calculated using the deconvolution of the V2p3/2 peak. The VPSB1 shown to have lowest yields for the V⁵⁺ contributions, revealing that this dopant dosage has a lower selectivity to the maleic anhydride. While VPSB5 on the other hand showed higher V^{5+} and V^{4+} contributions as compared to the others, which were 72 and 28%, respectively, with a vanadium oxidation state of 4.62. As compared to the undoped VPSU with 64% of V^{5+} and 36% of V^{4+} contributions, the VPSB5 demonstrated higher V⁵⁺ contribution, leading to better selectivity to maleic anhydride. A higher average oxidation state of vanadium was obtained due to addition of bismuth that promotes the formation of the V^{5+} phase in the catalyst. This is in agreement with the XRD and redox titration results that showed the presence of the V^{5+} phase and the higher average oxidation state with a higher concentration of V^{5+} .

As illustrated in Table 2, the V2p_{3/2} binding energy values of the VPSB1, VPSB3, and VPSB5 were 517.49, 517.86, and 517.87 eV, respectively, which were approximate to the value of the undoped catalyst, 517.58 eV. Hence, it can be suggested that the valence states of vanadium were in the range of 4-5 and the vanadium species in the synthesized catalysts were mainly in the form of $(VO)_2P_2O_7$ ^[4,23–27] As shown in Table 2, the P2p binding energies detected were almost the same among all of the samples, which revealed that the element of P was present on the surface, this phenomenon was good as the slight excess of phosphorus helps in stabilizing the V⁴⁺ oxidation state.^[29,30] As for the binding energies of oxygen, O1s, the values were very similar (532.0 eV) for all the samples, which were close to the reference, approx. 531 eV.^[4,24-27] The average oxidation state of vanadium was calculated and shown in Table 2, the range of which is 4.30 to 4.62.

2.3 | Field-emission scanning electron microscopy

The surface morphologies and particle sizes with different magnifications of the catalysts obtained from field-emission scanning electron microscopy (FE-SEM) are shown in Figure 3. The catalysts showed similar principal and secondary structures, consisting of different sizes of plate-like crystals with further agglomeration, forming more compact structures. However, unlike the conventional synthesized catalysts that show rosette-shape aggregates, ^[3,11,14] these crystallites exhibit much smaller fracturing pieces, stacking on each other. These agglomerates presumably are the (VO)₂P₂O₇ platelets that preferentially expose the (1 0 0) crystal plane.^[3,11] Abon et al reported the increase of the crystallinity of the (VO)₂P₂O₇ phase would change the morphology of the catalyst particles and bring about the

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FIGURE 2 XPS spectra obtained with monochromatic AlK α (1,486.74 eV) excitation with O1s,V2p_{1/2} and V2p_{3/2} photoelectron peaks and fitting curve for; (a) VPSU, (b)VPSB1, (c)VPSB3, and (d) VPSB5

formation of more split agglomerates.^[4] Although the Bidoped catalysts synthesized using the direct ultrasound technique do not agglomerate into the characteristic rosetteshape as the conventional Bi-doped catalysts,^[3] these catalysts still showed further agglomeration among the clusters with additional layered plate-like crystals at the surface of the clusters. The smaller and thinner clusters observed may be due to the cavitation effect of ultrasound during the synthesis process, which could have contributed to the increment in the surface area, leading to the increment in the exposure of the (1 0 0) reflection plane. As shown in Figure 3, the overall particle sizes of VPSB1, VPSB3, and VPSB5 were less than 1.0 µm, indicating that smaller crystallites are produced using the ultrasound irradiation technique. The reduction indicates that there will be increment in surface areas, which leads to more surface available for catalytic reactions, thus giving higher catalytic activity. The micrographs were also in good agreement with the results obtained from the XRD patterns where the increase in reflection intensity would bring out the formation of more split $(VO)_{2}P_{2}O_{7}^{[9,13,31]}$

2.4 | Chemical analysis

The composition of vanadium and the percentages of V^{5+} and V^{4+} oxidation states are summarized in Table 3. Chemical analysis using inductively coupled plasma-optical emission spectrometer (ICP-OES) indicated that all Bidoped catalysts exhibited a higher phosphorus content with the increase observed in the P/V atomic ratio from 1.11 (undoped) to 1.23 for VPSB1, 1.25 for VPSB3, and 1.26 for VPSB5. Compared to conventional Bi-doped catalysts,^[3] the increment of the P/V atomic ratio was less than 0.01 for the same dopant dosage applied, which indicates that a similar composition can be produced using the ultrasound technique in a shorter duration. The slightly higher P/V atomic ratio exhibited by the Bi-doped catalysts in the present study helps in stabilizing the V^{4+} oxidation and preventing the oxidation of $(VO)_2P_2O_7$. The chemical analyses further confirmed the presence of bismuth only in the doped catalysts with Bi/V atomic ratios of VPSB1, VPSB3, and VPSB5 shown to be 0.012, 0.032, and 0.047, respectively. The average oxidation numbers obtained were 4.34, 4.39, and 4.58 for VPSB1, VPSB3 and VPSB5, respectively. The average oxidation state slightly higher than 4.0 is associated with the P/V ratio slightly higher than 1.0, showing the characteristics of the $(VO)_2P_2O_7$ phase.^[3,4,14,21] The redox titration and XPS results are shown to have the same trend, and in the presence of Bi, the average oxidation number was found to be higher than that of the undoped catalyst. The average oxidation number was observed to be slightly higher than 4.0 due to the presence of V⁵⁺ species (shown in XRD and XPS profiles), as Bi promotes the formation of V^{5+} species.

	Binding energy (eV)					
Catalyst	V2p _{3/2}	P2p	O1s	Average oxidation state of vanadium $\left(V_{\text{ox}}\right)$	V ⁴⁺ (%)	V ⁵⁺ (%)
VPSU	517.58	133.99	531.97	4.03	36	64
VPSB1	517.49	133.61	531.49	4.30	61	39
VPSB3	517.86	133.61	531.52	4.53	44	56
VPSB5	517.87	133.60	531.40	4.62	28	72

$\label{eq:constraint} \textbf{T} \textbf{A} \textbf{B} \textbf{L} \textbf{E} ~ \textbf{2} \qquad \text{XPS results of } (VO)_2 P_2 O_7 \text{ catalysts}$

2.5 | X-ray absorption near edge structure (XANES) measurement of synthesized vanadium pyrophosphate catalysts

The X-ray absorption edge and pre-edge positions were used in this work to provide basic information on the different oxidation states of V (vanadium) in the as-synthesized catalysts to further understand the surface reaction mechanisms. The normalized V K-edge XANES patterns of the VPSU, VPSB1, VPSB3, and VPSB5 were determined using V³⁺, V^{4+} , and V^{5+} standards as presented in Figure 4. Three peaks above the absorption edge in the region 0-50 eV were used to obtain a better fitting of the absorption edge position in the spectra of both V standards and the as-synthesized catalysts. Based on these adsorption spectra, the pre-edge absorption positions of the V^{3+} , V^{4+} , and V^{5+} standards due to the 1 s-to-3d transition were determined to be 5,468.2, 5,469.1, and 5,470.7 eV, respectively. In addition, the inflection point of the V K-edge absorption, for oxidation states of 3+, 4+, and 5+, were 5,477.8, 5,479.6, and 5,482.2 eV, respectively. The pre-edge XANES spectra of V for the assynthesized catalysts exhibited an absorbance feature at the 1s-to-3d transition. As for the fresh catalyst samples, the sharp features were observed at 5,480-5,482 eV indicating that the fresh catalysts hold an oxidation state of V^{4+} or V^{5+} , and not V^{3+} . Due to the occurrence of vanadium oxide reduction in hydrogen gas flow, the shoulders at 5,490-5,494 eV were attributed to the dipole allowed, 1s-to-4pxy transition, which indicated the presence of V^{4+} and V^{5+} species in the as-synthesized catalysts. These adsorption spectra could be fitted well without any contribution from V³⁺.

2.6 | Temperature-programmed reduction in H_2/N_2

Temperature-programmed reduction (TPR) in H2 analyses were used to investigate the redox properties, the nature and the oxidising species available from the catalysts. The TPR results are shown in Figure 5, the total amount of oxygen removed from each peak, including the peak maxima temperatures and the derived reduction activation energy of the catalysts, are listed in Table 4. The Bi-doped catalysts showed three peak maxima in the reduction by H_2 (Figure 5). The first two peaks corresponded to the reduction of the V⁵⁺ phase, while the last peak corresponded to the removal of lattice oxygen from the active V⁴⁺ phase.^[3,14,21] The peak attributed to V⁴⁺ is associated with the removal of O⁻ anions and the peak from V⁵⁺ is related to the oxygen species of O^{2-.[3,4,14,21]}

The reduction patterns changed significantly with the addition of bismuth to the VPO catalyst, in which the reduction of V^{5+} species appeared to be predominant, whereas the reduction peak of V^{4+} was decreased. A similar trend was also reported^[8] in a previous study in which the Bi-doped catalysts were produced using the reflux conventional method^[3] and the Bi-Fe catalyst was produced using the reflux VPD method.

In comparison to the undoped catalyst, the reduction peaks occurred at lower temperature for the Bi-doped catalyst. First and second peaks of VPSB1 occurred at 790 and 819 K while the last peak appeared at 1138 K with the amount of oxygen removed from V⁵⁺ was significantly increased to 7.57×10^{20} and the amount of oxygen removed from V^{4+} was 4.54×10^{20} atom/g, respectively. The ratio of oxygen atoms removed from V⁵⁺/V⁴⁺ was 1.67. Similarly, VPSB3 gave three peaks appearing at 788, 850, and 1131 K. The reduction peaks generally shifted to a lower temperature with an increase of Bi concentration. Total oxygen species from V^{5+} removed species was reduced to 1.99×10^{20} atom/g, whereby the oxygen removed from V⁴⁺ species was also decreased to 2.54×10^{20} atom/g. The phenomenon of reduction of reactivity in bismuth 3 mol% was also reported by Leong et al using a conventional preparation method of the Bi-doped catalyst.^[3] The first two peaks of VPSB5 appeared at slightly higher temperature than VPSB1 and VPSB3, that is, 856 and 1149 K with the third peak occurring at 1195 K. The removal of oxygen species linked to V^{5+} and V^{4+} species have tremendously increased to 2.54×10^{21} atom/g and 1.49×10^{21} atom/g, respectively. As a result, the ratios of oxygen species removed were increased. Hence, among the Bi-doped catalysts produced via the ultrasound technique, VPSB5 probably demonstrated the highest reactivity.





(b)



(c)



(d)



FIGURE 3 FE-SEM micrographs of (a) VPSU, (b) VPSB1, (c) VPSB3, and (d) VPSB5 catalysts

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The Bi-doped catalysts produced using the direct ultrasound method in general exhibited the reduction peaks at a lower temperature, thus leading to more labile oxygen, which consequently resulted in a higher removal of oxygen species that was attributed to the activity of the catalyst. Besides, the results shown by TPR in H₂ analyses also indicated that the introduction of increasing concentration of Bi promoter would lead to the increment of the amount of oxygen species associated with V⁵⁺ species with slight impact. These results were in agreement with the results of XRD and XPS, which also showed the presence of higher amounts of V⁵⁺.

2.7 | Selective oxidation of *n*-butane to maleic anhydride

The catalytic performances of VPO catalysts for oxidation of *n*-butane to maleic anhydride were tested at a typical operating temperature of 673 K (Table 5). The undoped catalyst synthesized using the direct ultrasound method showed a conversion of *n*-butane of 58%, the doped catalysts have shown a conversion of *n*-butane of 45, 50, and 65% for VPSB1, VPSB3, and VPSB5, respectively. As compared to the conventionally prepared Bi-doped catalysts,^[3] there was an increment observed in the catalytic activity. However, compared to the undoped catalyst produced using the direct ultrasound method, addition of higher amounts of bismuth better improves the catalytic activity. The VPSB1 and the undoped catalyst showed the same maleic anhydride selectivity, 68%, respectively. Further addition of bismuth had increased the catalyst selectivity to 73 and 80% for VPSB3 and VPSB5, respectively. These observations indicated that the introduction of a higher amount of Bi into the catalysts improved catalyst selectivity toward maleic anhydride.

3 | EXPERIMENTAL

3.1 | Catalyst preparation

The catalysts were prepared via sesquihydrate route and direct ultrasound method, wherein V_2O_5 (15 g) was mixed with aqueous 85% *ortho*-phosphoric acid (90 mL) and distilled water (360 mL). The mixture was subjected to direct ultrasound irradiation (40% amplitude) for 1 hr by an ultrasonic probe (2.0 cm diameter) using a 750 W, 20 kHz Ultrasonic Power Supply from SnapTec NexTgen (Model 10000-03). The power supply features an automatic amplitude and frequency control circuitry that eliminates the need for constant adjustments and assures optimum cavitation at any power level. The tip of the ultrasonic probe was immersed \sim 2 cm below the surface of the mixture (Figure 6) and the catalyst remained suspended in the

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TABLE 3 Chemical compositions, average oxidation numbers, and percentages of V^{4+} and V^{5+} oxidation states present in doped VPO catalysts

		Inductively coupled plasma				
Catalyst	Energy-dispersive X-ray	P/V	Bi/V	V ⁴⁺ (%)	V ⁵⁺ (%)	Average oxidation number
VPSU	1.66	1.11	_	72.22	27.78	4.2778
VPSB1	1.34	1.23	0.012	65.57	34.43	4.3443
VPSB3	1.52	1.25	0.032	60.89	39.11	4.3911
VPSB5	1.62	1.26	0.047	42.25	57.75	4.5775



FIGURE 4 The V K–edge-normalized XANES of VPSU, VPSB1, VPSB3, and VPSB5 catalysts



FIGURE 5 TPR in H_2 profiles of undoped and Bi-doped catalysts

absence of any external mixing due to the acoustic effect of ultrasound waves. The brownish solid solution (color of V_2O_5) gradually changed to yellow. The solid (VOPO₄·2H₂O) was recovered by centrifugation and was oven dried at 353 K overnight. Next, the well-synthesized VOPO₄·2H₂O (10 g) was subjected to direct ultrasound

irradiation for 1 hr with 1-butanol (50 mL) and bismuth nitrate, Bi(NO₃)₃·2H₂O as the salt of the promoter. At this stage, bismuth was added according to the mole percentage of the dopant (1, 3 and 5%). The resulting light blue solid (VOHPO₄·1.5H₂O precursor) was recovered by centrifugation and washed sparingly with acetone, further oven dried at 353 K overnight. The obtained precursors were calcined under a flow of 0.75% *n*-butane in air mixtures at 673.15 K (400°C) for 24 hr to produce the active catalysts, (VO)₂P₂O₇. The activated Bi-doped (1, 3 and 5%) catalysts were denoted as VPSB1, VPSB3, and VPSB5, respectively. The same method was used to prepare the undoped catalyst, denoted as VPSU.

3.2 | Catalyst characterization

The XRD analyses were carried out using a Shimadzu diffractometer model XRD 6000 employing Cu Ka radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The estimation of the crystallite size based on X-ray peak broadening is carried out using the Debye-Scherrer equation. The FWHM of the (0 2 0) and (2 0 4) planes were used to determine the crystallite size of the catalysts. The parameter used to determine the crystal size of the catalysts is the half width of the (0 2 0) reflection. The thickness of the (2 0 4) plane is indicative of the mean "length" at the $(2\ 0\ 4)$ face, while the thickness of $(0\ 2\ 0)$ is representative of the actual thickness.^[2,3,6,14,21] Therefore, the line width increases with the decrease in the crystallite size. The chemical composition on the surface of the catalyst was determined using XPS (Physical Electronic ESCA PHI 1600) at an excitation energy of Al K α (1,486.6 eV). The C1s (284.5 eV) peak was used as the calibration standard for the wide-region spectra of the vanadium and phosphorus species. The XPS signals of the above species were recorded with a cylindrical mirror analyzer. In the present practice, the peak deconvolution procedure where VOPO₄ (oxidation state, +5) with phase structure confirmed by XRD results provided the reference value for the binding energy of the $V2p_{3/2}$ peak. The measured $V2p_{3/2}$ peak (FWHM < 1.3 eV) could be well fitted with a single Gaussian with a maximum

Catalyst	T _{onset} (K)	Peak	T _{max} (K)	Reduction activation energy, E_r (kJ/mol)	Oxygen removed (atom/g)	Ratio of oxygen removal from V ⁵⁺ /V ⁴⁺
VPSU	752	1	981	408	4.69×10^{20}	0.26
		2	1158	482	1.78×10^{21}	
	Total oxygen	removed:			2.25×10^{21}	
VPSB1	593	1	790	329	1.58×10^{20}	1.67
		2	819	341	5.99×10^{20}	
		3	1138	473	4.54×10^{20}	
	Total oxygen	removed:			1.21×10^{21}	
VPSB3	669	1	788	328	1.05×10^{20}	0.79
		2	850	354	9.37×10^{19}	
		3	1131	470	2.54×10^{20}	
	Total oxygen	removed:			4.53×10^{20}	
VPSB5	672	1	856	356	1.18×10^{21}	1.71
		2	1149	478	1.36×10^{21}	
		3	1195	497	1.49×10^{21}	
	Total oxygen	removed:			4.03×10^{21}	

TABLE 4 Total number of oxygen atoms removed, values of reduction activation energy, and the ratio of oxygen removal from V^{5+}/V^{4+} and V^{4+}/V^{5+} obtained by the reduction in H₂/N₂ for Bi-doped catalysts

TABLE 5 Catalytic performances of undoped and doped VPO catalysts

		Catalyst selectivity (%)	
Catalyst	<i>n</i> -butane conversion (%)	MA	CO/CO ₂
VPSU	58	68	32
VPSB1	45	68	32
VPSB3	50	73	27
VPSB5	65	80	20



FIGURE~6 $\ \ \,$ The tip of the ultrasonic probe was immersed ${\sim}2$ cm below the surface of the mixture

at 518 eV.^[4,23–27] The morphologies, microstructures, and particle sizes of the catalysts were investigated using a FE-SEM (Hitachi, S-4700 Type II). Energy-dispersive X-ray (EDX) analyses were carried out using EDAX software. The

bulk chemical composition was determined using a sequential scanning ICP-OES (Perkin Elmer Emission Spectrometer model Plasma 1000). The average oxidation states of vanadium in all the catalysts were determined by redox titration following the method of Niwa and Murakami.^[32] The XANES spectra were collected on the Wiggler beam line 16A1 at the National Synchrotron Radiation and Research Center in Taiwan. Data were collected in the transmission mode using a Lytle detector in the regions of V K-edges at room temperature. The data were subsequently normalized using Athena (vi) software. TPR in H₂ analysis was done using a Thermo Electron TPDRO 1100 apparatus utilizing a thermal conductivity detector. The catalyst was pretreated in a flow of 20 cm³/ min purified nitrogen, held for 10 mins before cooling to ambient temperature. Sample analysis was done at a flow of 5.5% hydrogen in nitrogen (25 cm³/min), starting from room temperature to 1000°C with a heating ramp of 5°C/min.

3.3 | Selective oxidation of *n*-butane to maleic anhydride

The oxidation of *n*-butane was carried out in a fixed-bed microreactor at 673 K with gas hourly space velocity $(GHSV) = 2,400 \text{ hr}^{-1}$ with a standard mass of the catalyst (250 mg). A mixture of 1.0% *n*-butane and air was fed to the reactor via a calibrated mass flow controller. The products were then fed via heated lines to an on-line gas chromatography for analysis. The reactor comprised a 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 control was typically ± 1 K. Carbon mass balances of $\geq 95\%$ were typically observed.

4 | CONCLUSIONS

It is shown in this study that all the bismuth-promoted $(VO)_2P_2O_7$ phase produced via direct ultrasound synthesis contains higher V⁵⁺ with a smaller particle size, thereby indicating better catalytic performances with higher selectivity to maleic anhydride. The ultrasound irradiation technique further improved the catalytic performances by increasing the surface area with better topographical morphologies. The Bi-doped catalysts synthesized using the direct ultrasound technique were shown to be of crystals having thinner and smaller plate-like structures. The V2p_{3/2} binding energy analyses further concreted the findings of the diffractogram of XRD, in which the Bi-doped catalysts exhibited good crystallinity with characteristic peaks of the $(VO)_2P_2O_7$ catalysts. The preparation of Bi-doped catalysts through the ultrasound synthesis technique has drastically reduced the synthesis time to only 2 hr compared to the conventional 32–48 hr.^[3,8,11–14]

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