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The effect of Bi promoter on vanadium phosphate catalysts synthesized via sesquihydrate route

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ABSTRACT

A series of 1%, 3% and 5% Bi-doped vanadyl pyrophosphate catalysts were prepared via sesquihydrate route (VPO_s method). These catalysts were denoted as VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5%. Bulk and Bi-promoted vanadyl pyrophosphate catalysts prepared via sesquihydrate route exhibited a well-crystallized $(VO)_2P_2O_7$ phase. Two V^{5+} phases, *i.e.* β-$VOPO_4$ and α_{II}-$VOPO_4$ were observed in all Bi-promoted VPO catalysts, which led to an increase in the specific surface area and average oxidation state of vanadium. Bi-promoted VPO catalysts showed six to nine times higher amounts of oxygen evolved than the bulk VPO catalyst in oxygen TPD and a significant shift in the reduction peaks to lower temperatures. Catalytic tests revealed that both activity and selectivity to maleic anhydride increased with the presence of bismuth promoter.

1. Introduction

Vanadium phosphorus oxides (VPO) were found to be effective catalysts to synthesize maleic anhydride from *n*-butane. Currently, this is the only successful industrial application of alkane selective oxidation by heterogeneous gas–solid catalytic processes [1,2]. The active and selective phase of the VPO catalyst responsible for this reaction is vanadyl pyrophosphate, $(VO)_2P_2O_7$ [3].

Almost all the industrial catalysts for oxidation reactions contain promoters of different kinds. Promoters which are added can act specifically as textural promoters or enhance the activity as well as the selectivity of the bulk catalyst [4,5]. A wide range of cations such as Ce, Cd, Ni, Zn, Bi, Cu, Li, V, Zr, Mg, Ti, La, Mo, Nb, B, Fe and Cr have been mainly reported in patents [4], although a few articles have been published in the open literature. Hutchings and Higgins [6] tested a range of promoter elements and concluded that only Co and Mo showed promotional effect while others are promoters which only responsible for an increase in surface area of $(VO)_2P_2O_7$.

One of the most intensively studied dopants for VPO catalysts for the past two decades is bismuth. Some researchers have claimed that addition of bismuth into VPO increases the selectivity to maleic anhydride [7–9]. However, Bi-doped catalysts prepared via VPD method showed an enhancement of the activity of the catalyst instead [10]. Recently, Bi-doped VPO catalysts prepared via mechanosynthesis and mechanochemical treatment were also reported [11].

In this study, the undoped and Bi-doped VPO catalysts were prepared via vanadyl hydrogen phosphate sesquihydrate precursor ($VOHPO_4{\cdot}1.5H_2O$), denoted as the VPO_s route. The effect of different percentages of bismuth promoter towards the physicochemical properties and catalytic performance of the VPO catalysts was examined.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared via dihydrate method employing the sesquihydrate route. Vanadium (V) oxide, V_2O_5 (15.0 g from Merck), was suspended with continuous stirring into a mixture of *ortho*-phosphoric acid, *o*-H_3PO_4 (90 ml, 85% from Merck) and distilled water (24 ml g^{-1} solid). This mixture was stirred and refluxed at 393 K for 24 h. Then, the mixture was cooled to room temperature and the resulting yellow solid ($VOPO_4{\cdot}2H_2O$) was recovered by centrifugation and oven-dried at 358 K for 72 h. After that, the well synthesized $VOPO_4{\cdot}2H_2O$ (10.0 g, 50.5 mmol) was refluxed for 8 h with 1-butanol (150 ml from Merck) and bismuth nitrate, $Bi(NO_3)_3{\cdot}5H_2O$ (from Sigma) as the salt of the promoter. In this step, bismuth was added according to the percentage of dopant (1%, 3% and 5%). The resulting light blue solids ($VOHPO_4{\cdot}1.5H_2O$ precursors) were recovered by centrifugation and washed sparingly with a small amount of acetone and then oven-dried at 358 K for 72 h. The precursors were denoted as VPO_s-Bi1%pre, VPO_s-Bi3%pre and VPO_s-Bi5%pre for 1%, 3% and 5% of Bi doping, respectively. The undoped precursor was prepared using the same method mentioned above without the addition of the promoter.

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The precursors obtained were then calcined in a reaction flow of 0.75% *n*-butane in air mixture at 733 K for 18 h to generate the active catalysts, $(VO)_2P_2O_7$. The activated Bi-doped (1%, 3% and 5%) catalysts were denoted as VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5%, respectively.

2.2. Catalysts characterisation

The X-ray diffraction (XRD) patterns were obtained by using a Shimadzu model XRD-6000 Diffractometer employing Cu K_α radiation to generate diffraction patterns from powder crystalline samples at ambient temperature.

The total surface area of the catalysts was measured by Brunauer–Emmett–Teller (BET) method by using nitrogen adsorption at 77 K. This was done by using a Thermo Finnigan Sorptomatic 1990 nitrogen adsorption–desorption analyser.

The bulk chemical composition was determined by using a sequential scanning inductively coupled plasma-optical emission spectrometer (ICP-OES) Perkin Elmer Optical Emission Spectrometer Optima 2000 DV.

The average oxidation states of the vanadium in all the catalysts were determined by redox titration following the method of Niwa and Murakami [12].

Scanning electron microscopy (SEM) analyses were done by using a Supra 55VP electron microscope. Energy-dispersive X-ray (EDX) analyses were carried out by using EDAX software.

Temperature-programmed desorption (TPD) of O_2 and temperature-programmed reduction (TPR) in H_2 analyses were done by using a Thermo Electron TPDRO 1100 apparatus utilising a thermal conductivity detector (TCD).

2.3. 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 GHSV = 2400 h^{-1} with a standard mass of catalyst (250 mg). A mixture of 1.0% *n*-butane and air was fed to the reactor via 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 centre of the catalyst bed and temperature control was typically ±1 K. Carbon mass balances of ≥95% were typically observed.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The XRD patterns of the undoped and Bi-doped catalysts calcined at 733 K in a reaction flow of *n*-butane in air mixture for 18 h are shown in Fig. 1. The diffractogram of the undoped catalyst showed similar diffraction pattern comprised of a well-crystallized $(VO)_2P_2O_7$ phase with the main characteristic peaks appeared at $2\theta = 22.9^\circ$, 28.4° and 29.9° (JCPDS File No. 34-1381), which corresponded to the reflection of (0 2 0), (2 0 4) and (2 2 1) planes, respectively.

However, Bi-doped catalysts were found to consist a mixture of $(VO)_2P_2O_7$ and some V^{5+} phases, *i.e.* β-$VOPO_4$ (JCPDS File No. 27-0948) observed at $2\theta = 21.5^\circ$ and α_{II}-$VOPO_4$ (JCPDS File No. 34-1247) observed at $2\theta = 25.1^\circ$ and 29.3°. These peaks belonging to the various V^{5+} phases were shown to be more intense as the percentage of doping increased indicating that addition of bismuth promotes the formation of V^{5+} phase in the catalysts. This is in agreement with the redox titration results which showed that Bi-doped catalysts gave higher average oxidation state with high concentration of V^{5+} than undoped catalyst as to be discussed in Section 3.2.

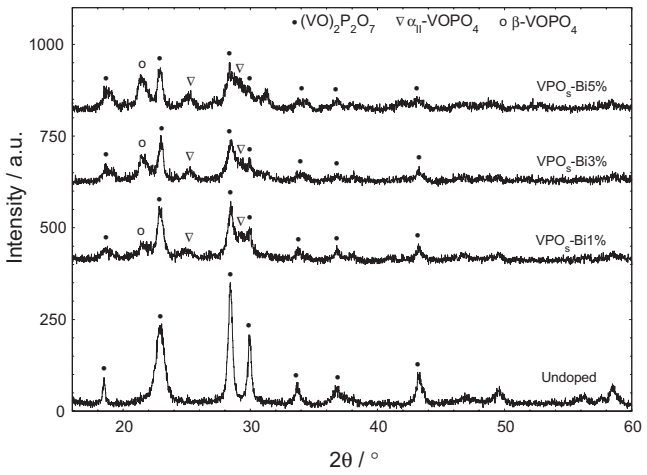

Fig. 1. XRD patterns of undoped and Bi-doped VPO_s catalysts.

The addition of Bi has led to the reflection peaks at all the three major peaks ($2\theta = 22.9^\circ$, 28.4° and 29.9°) indexed to the (0 2 0), (2 0 4) and (2 2 1) planes being less intense with broader width sizes for the Bi-doped catalysts as compared to the undoped catalyst and the intensity of these peaks further reduced as the amount of doping increased from 1% to 5%. The estimation of the crystallite size based on X-ray peaks broadening is calculated by using the Debye–Scherrer equation:

$$t = \frac{0.89\lambda}{\beta_{h\ k\ l}\cos\theta_{h\ k\ l}}$$

where t is the crystallite size for ($h\,k\,l$) phase, λ is the X-ray wavelength of radiation for Cu K_α, $\beta_{h\,k\,l}$ is the full-width at half maximum (FWHM) at ($h\,k\,l$) peak and $\theta_{h\,k\,l}$ is the diffraction angle for ($h\,k\,l$) phase [13].

The FWHM of the (0 2 0) and (2 0 4) planes are used to determine the crystallite size of the catalysts. The line width increases with the decreasing size of the crystallites [14]. The decrease in the FWHM of the (0 2 0) reflection indicates that the thickness of the particles in the (1 0 0) direction decreases. The incorporation of bismuth into the VPO_s catalysts have shown to produce catalysts with larger crystallite sizes in the (0 2 0) direction but smaller crystallite sizes in the (2 0 4) direction as compared to the undoped catalyst. These results were in contrary with the case of the Bi-doped $(VO)_2P_2O_7$ catalysts obtained via VPD method [11,15]. As tabulated in Table 1, the crystallite sizes of (0 2 0) reflection plane for undoped, VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5% were calculated as 108.28 Å, 149.21 Å, 187.78 Å and 118.40 Å, respectively, whereas the crystallite sizes of (2 0 4) reflection plane for the same series of catalysts produced were 209.37 Å, 132.79 Å, 114.41 Å and 44.02 Å, respectively.

3.2. BET surface area measurements and chemical analyses

The surface area of the Bi-doped catalysts are as follows: 29 $m^2\,g^{-1}$ for VPO_s-Bi1%, 22 $m^2\,g^{-1}$ for VPO_s-Bi3% and 21 $m^2\,g^{-1}$ for VPO_s-Bi5% (Table 2). As compared to the undoped catalyst (19 $m^2\,g^{-1}$), the Bi-doped catalysts have shown higher specific surface area. This suggests that bismuth has acted as a good structural promoter as it has somehow intercalated into the VPO_s structure and altered the development of the basal (1 0 0) plane, which led to the increase of surface area of the catalysts. Evidence was shown by the secondary electron images from SEM micrographs and discussed in the following section. This interesting phenomenon was also observed in a previous report [15].

Table 1
XRD data of undoped and doped VPO_s catalysts.

Catalyst	Line width[a] (0 2 0) (°)	Line width[b] (2 0 4) (°)	Crystallite size[c] (0 2 0) (Å)	Crystallite size[c] (2 0 4) (Å)
Undoped	0.7400	0.3869	108.28	209.37
VPO_s-Bi1%	0.5370	0.6100	149.21	132.79
VPO_s-Bi3%	0.4267	0.7080	187.78	114.41
VPO_s-Bi5%	0.6767	1.8400	118.40	44.02

[a] FWHM of (0 2 0) reflection plane.
[b] FWHM of (2 0 4) reflection plane.
[c] Crystallite thickness by means of the Debye–Scherrer formula.

Table 2
Specific BET surface areas, chemical compositions, average oxidation numbers and percentages of V^{4+} and V^{5+} oxidation states present in undoped and doped VPO_s catalysts.

Catalyst	Specific BET surface area ($m^2\,g^{-1}$)	EDX	ICP		V^{4+} (%)	V^{5+} (%)	Average oxidation number
			P/V	Bi/V			
Undoped	19	1.12	1.03	–	95.81	4.19	4.0419
VPO_s-Bi1%	29	1.13	1.21	0.008	54.19	45.81	4.4581
VPO_s-Bi3%	22	1.23	1.22	0.028	58.80	41.20	4.4120
VPO_s-Bi5%	21	1.05	1.25	0.047	49.74	50.26	4.5026

Chemical analyses using ICP-OES indicated that all Bi-doped catalysts had higher phosphorus content due to an increase in the P/V atomic ratio from 1.03 (undoped) to 1.21 for VPO_s-Bi1%, 1.22 for VPO_s-Bi3% and 1.25 for VPO_s-Bi5%. As for the EDX analyses, results showed that the P/V atomic ratio were in between 1.05 and 1.23 (Table 2). The results were in close agreement with the optimal P/V atomic ratio range for producing the $(VO)_2P_2O_7$ phase [3]. Chemical analyses confirmed the presence of Bi in the doped catalysts with Bi/V atomic ratios of 0.008, 0.028 and 0.047 for VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5%, respectively. The average oxidation numbers of the vanadium and percentage of V^{5+} and V^{4+} oxidation states are summarised in Table 2. The doping of different percentages of Bi promoter has drastically increased the amount of V^{5+} contribution from 4.19% for undoped to 45.81%, 41.20% and 50.26% for VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5%, respectively. As a result, the average oxidation number of the vanadium has increased from 4.0419 for undoped to 4.4581, 4.4120 and 4.5026 for the same series of Bi-doped VPO_s catalysts. The increment in the average oxidation state of the vanadium is due to the presence of a V^{5+} phases, as shown by the XRD profiles.

3.3. Scanning electron microscopy (SEM)

The surface morphologies of the undoped and Bi-doped catalysts retrieved by scanning electron microscopy (SEM) are shown in Fig. 2(a)–(d). These catalysts showed similar principle secondary structures, consisting different sizes of plate-like crystals, which were agglomerated into the characteristics of rosette-shape clusters. These plate-like crystallites are comprised of agglomerates of $(VO)_2P_2O_7$ platelets that preferentially exposing the (1 0 0) crystal plane [16]. $(VO)_2P_2O_7$ catalysts obtained via conventional organic and dihydrate methods could also find similar type of platelet arrangement [16–19].

Bi-doped catalysts (Fig. 2(b)–(d)) show more compact structures with further agglomeration among the rosette-shape clusters and additional layered plate-like crystals which are formed at the surface of clusters. The size of these rosette-shape clusters observed is smaller than the undoped counterpart. This effect could have contributed to the increase in surface area of the Bi-doped catalysts as found in the BET surface area measurements. The layered structure has brought about increment in the exposure of the basal (1 0 0) reflection plane. This interesting phenomenon is also observed in the Bi-doped catalysts prepared via VPD method employing the hemihydrate route [15].

3.4. Temperature-programmed desorption (TPD) of O_2

The TPD of O_2 profiles of the undoped and Bi-doped catalysts shown in Fig. 3 were obtained by pretreating the fresh catalysts by heating them to 673 K in an oxygen flow (1 bar, 25 $cm^3\,min^{-1}$) and held at 673 K for 30 min in the same stream before cooling to ambient temperature. Then, the flow was switched to helium (1 bar, 25 $cm^3\,min^{-1}$) and the temperature was raised to 1173 K. The peak maxima temperatures, the amount of desorbed oxygen and the derived desorption activation energies are summarised in Table 3.

The undoped catalyst gave a broad and weak peak with a peak maximum at 954 K. However, doping 1% Bi into the catalyst gave a peak maximum, which occurred at a lower temperature, *i.e.* 948 K. VPO_s-Bi3% gave the most intense peak comparatively with a peak maximum at 975 K. As the doping of Bi increased to 5%, the peak maximum for the catalyst has occurred at 963 K. These are assigned to the lattice oxygen, which also has been found earlier in the VPO catalyst prepared via organic and dihydrate method [20]. The addition of lower amount of Bi (*i.e.* 1%) had reduced the lattice oxygen desorption temperature but this do not apply for higher levels of doping.

Comparatively, Bi-doped catalysts have higher total amount of oxygen desorbed (Table 3) from the catalysts than the undoped counterpart. The total amount of oxygen desorbed

Table 3
Total amount of oxygen atoms desorbed and values of desorption activation energies obtained by temperature programmed desorption for the undoped and doped VPO_s catalysts.

Catalyst	T_m (K)	Desorption activation energy, E_d ($kJ\,mol^{-1}$)	Total amount of oxygen desorbed ($mol\,g^{-1}$)	Total amount of oxygen desorbed ($atom\,g^{-1}$)
Undoped	954	263.4	6.99×10^{-5}	4.21×10^{19}
VPO_s-Bi1%	948	261.8	4.67×10^{-4}	2.81×10^{20}
VPO_s-Bi3%	975	269.2	6.12×10^{-4}	3.68×10^{20}
VPO_s-Bi5%	963	265.9	5.81×10^{-4}	3.50×10^{20}

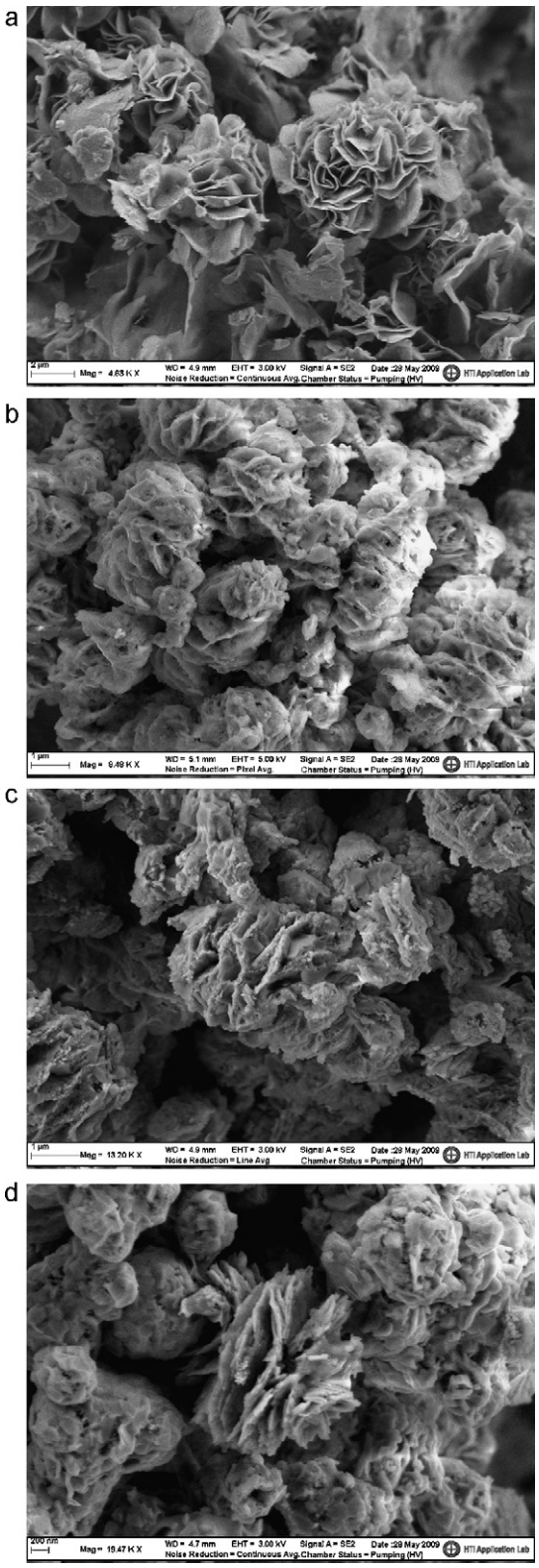

Fig. 2. SEM micrographs of (a) undoped, (b) VPO_s-Bi1%, (c) VPO_s-Bi3% and (d) VPO_s-Bi5% catalysts.

from undoped catalyst was 4.21×10^{19} atom g^{-1}. Addition of Bi promoter into the catalysts increased the total amount of oxygen desorbed to 2.81×10^{20} atom g^{-1}, 3.68×10^{20} atom g^{-1} and 3.50×10^{20} atom g^{-1} for VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5%, respectively. These results are supported by the increase of the

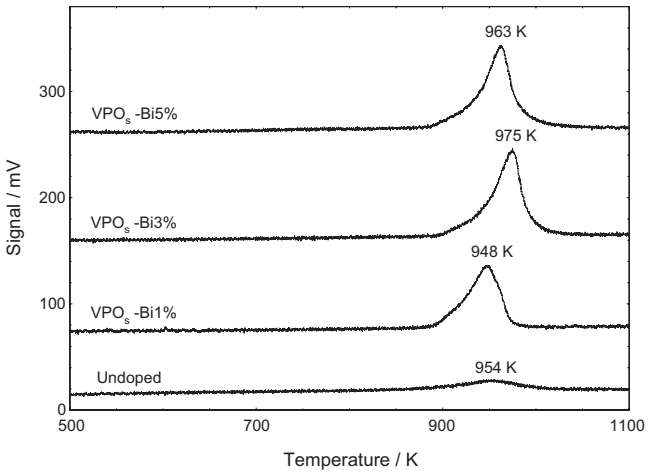

Fig. 3. TPD of O_2 profiles of undoped and Bi-doped VPO_s catalysts.

average oxidation number of vanadium (Table 2), which is due to the additional V^{5+} phase as confirmed by redox titration (Section 3.2).

3.5. Temperature-programmed reduction (TPR) in H_2/N_2

TPR in H_2 analyses were used to investigate the redox properties of the catalysts. Additional information as to the nature and the oxidising species available from the catalysts could be obtained. Fig. 4 shows the TPR profiles of undoped and Bi-doped VPO_s catalysts in H_2/N_2 stream (5% H_2 in N_2, 1 bar, 25 cm^3 min^{-1}) using a fresh sample of catalyst and raising the temperature from ambient to ~1173 K at 5 K min^{-1} in that stream. Table 4 lists the peak maxima temperatures, the amount of removed oxygen in each peak and the derived reduction activation energies.

The undoped and Bi-doped catalysts gave three peak maxima in the reduction by H_2 (Fig. 4). The first two peaks corresponded to the reduction of V^{5+} phase, whereas the third peak is assigned to the removal of lattice oxygen from the active V^{4+} phase [21,22]. The peak attributed to V^{4+} is associated to the removal of O^- anion and the peak from V^{5+} is related to the oxygen species of O^{2-} [21,23]. The reduction of V^{4+} species appeared to be the major peak for the undoped catalyst and this indicated that V^{4+} is the predominant species in the catalyst as shown by the redox titration. The undoped catalyst gave three peak maxima in the rate of hydrogen consumption at 744, 847 and 1005 K with the amount of oxygen removed

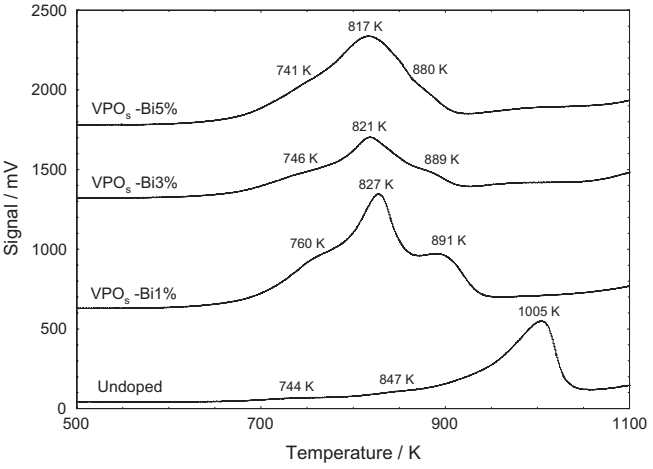

Fig. 4. TPR in H_2 profiles of undoped and Bi-doped VPO_s catalysts.

Table 4
Total amount of oxygen atoms removed, values of reduction activation energies and ratio for oxygen removal of V^{5+}/V^{4+} and V^{4+}/V^{5+} by reduction in H_2/N_2 for the undoped and doped VPO_s catalysts.

Catalyst	Peak	T_m (K)	Reduction activation energy, E_r (kJ mol^{-1})	Amount of oxygen removed (mol g^{-1})	Amount of oxygen removed (atom g^{-1})	Ratio for oxygen removal of V^{5+}/V^{4+}	Ratio for oxygen removal of V^{4+}/V^{5+}
Undoped	1	744	124.4	3.53×10^{-4}	2.13×10^{20}		
	2	847	141.6	4.21×10^{-4}	2.53×10^{20}		
	3	1005	168.1	3.38×10^{-3}	2.04×10^{21}		
	Total			4.16×10^{-3}	2.50×10^{21}	0.23	4.37
VPO_s-Bi1%	1	760	127.0	2.2504×10^{-3}	1.3547×10^{21}		
	2	827	138.2	2.9353×10^{-3}	1.7671×10^{21}		
	3	891	148.9	1.4838×10^{-3}	8.9325×10^{20}		
	Total			6.6695×10^{-3}	4.0151×10^{21}	3.49	0.29
VPO_s-Bi3%	1	746	124.7	8.9871×10^{-4}	5.4102×10^{20}		
	2	821	137.2	1.6655×10^{-3}	1.0026×10^{21}		
	3	889	148.6	6.1129×10^{-4}	3.6800×10^{20}		
	Total			3.1755×10^{-3}	1.9116×10^{21}	4.19	0.24
VPO_s-Bi5%	1	741	123.8	1.3785×10^{-3}	8.2986×10^{20}		
	2	817	136.5	3.0461×10^{-3}	1.8338×10^{21}		
	3	880	147.1	8.1508×10^{-4}	4.9068×10^{20}		
	Total			5.2397×10^{-3}	3.1543×10^{21}	5.43	0.18

in each peak is 2.13×10^{20}, 2.53×10^{20} and 2.04×10^{21} atom g^{-1}, respectively. The ratio of oxygen atoms removed from V^{5+}/V^{4+} is about 0.23.

By introducing Bi into VPO_s catalyst, the reduction patterns have changed significantly with the reduction of V^{5+} species appeared to be predominant, whereas the reduction peak of V^{4+} was tremendously decreased. This trend was similarly observed in previous report whereby Bi–Fe additive were incorporated during the reflux of dihydrate with isobutanol to produce the catalyst precursor [24]. VPO_s-Bi1% gave similar characteristic of three reduction peaks with undoped catalyst. The first peak occurred at higher temperature at 760 K while the second peak slightly shifted to a lower temperature, *i.e.* 827 K. However, the third reduction peak is significantly shifted to a lower temperature, *i.e.* 891 K. The removal amount of oxygen species associated with V^{5+} greatly increased to 3.12×10^{21} atom g^{-1}. The amount of oxygen removed from the third peak, which is assigned to the reduction of V^{4+} phase decreased to 8.93×10^{20} atom g^{-1}. Hence, the ratio of oxygen atoms removed from V^{5+}/V^{4+} is significantly increased to 3.49. Higher oxygen species associated to V^{5+} phase removal suggested that the catalyst tend to show a higher selectivity, which will be discussed in the following section.

As compared to VPOs-Bi1%, VPO_s-Bi3% gave three smaller peaks, which appeared at 746, 821 and 889 K. Increasing the amount of Bi in the VPO_s catalysts shifted all the three reduction peaks to lower temperatures. Besides, the third peak which is associated to the reduction of V^{4+} species has shown to be shifted nearer towards the second peak which is assigned to the reduction of V^{5+}. The oxygen species linked to V^{5+} phase was reduced to 1.54×10^{21} atom g^{-1}, whereas the oxygen removed from V^{4+} phase was also decreased to 3.68×10^{20} atom g^{-1}. The ratio of oxygen atoms removed from V^{5+} relative to that from the V^{4+} phase is further increased to 4.19.

As for the VPO_s-Bi5% catalyst, all the three reduction peaks appeared at lower temperatures, *i.e.* at 741, 817 and 880 K. The removal of oxygen species linked to V^{5+} and V^{4+} phases have increased to 2.66×10^{21} atom g^{-1} and 4.91×10^{20} atom g^{-1}, respectively. These results consequently increased the ratio for oxygen species of V^{5+}/V^{4+} to about 5.43. TPR in H_2 analyses results had indicated that the addition of increasing amounts of Bi promoter would lead to the enhancement of the amount of oxygen species associated with V^{5+} with slight effect on the amount of oxygen species associated with V^{4+} phase.

3.6. Selective oxidation of n-butane to maleic anhydride

The catalytic performance of the catalysts for *n*-butane oxidation to maleic anhydride (MA) has been tested at 673 K, a typical operating temperature for VPO catalysts. The details of the catalytic performance data of the undoped and Bi-doped catalysts are shown in Table 5. It is revealed that the incorporation of Bi into the catalyst system had increased the activity and selectivity of *n*-butane. The undoped catalyst has shown a conversion of *n*-butane of 20%. As compared to the undoped catalyst, Bi-doped catalysts showed higher conversion of *n*-butane, *i.e.* 29%, 28% and 29% for VPO_s-Bi1%, VPO_s-Bi3% and VPO_s-Bi5%, respectively. These results showed that the addition of higher amounts of Bi will not further improve the activity of the catalysts. The undoped catalyst showed 67% MA selectivity. As for the VPO_s-Bi1%, the MA selectivity remained unchanged. Further addition of Bi into the catalysts had enhanced the selectivity of the catalysts to 73% and 86% for VPO_s-Bi3% and VPO_s-Bi5%, respectively. These results indicated that the addition of increasing amounts of Bi into the catalyst had improved the selectivity of the catalyst towards MA. Although the V^{4+} species in Bi-doped catalysts were lower than the undoped counterpart, the conversion of all Bi-doped VPOs catalysts were shown to have higher conversion owing to their higher surface areas as analysed by BET measurements. Also, higher amount of V^{5+} species in the Bi-doped catalysts proved to have favoured the selectivity of the catalysts.

Table 5
Catalytic performances of undoped and doped VPO_s catalysts.

Catalyst	*n*-Butane conversion (%)	Product selectivity (%)		
		MA	CO	CO_2
Undoped	20	67	1	32
VPO_s-Bi1%	29	67	1	32
VPO_s-Bi3%	28	73	1	26
VPO_s-Bi5%	29	86	1	13

4. Conclusions

Bi-promoted catalysts gave better catalytic performances with high selectivity of the vanadium phosphate catalysts synthesized via sesquihydrate route. Bi-doped catalysts contained high V^{5+} species, which led to high selectivity of the catalysts. Bi was found to be a good structural promoter as it increased the specific surface area of the VPO_s catalyst. All catalysts exhibited good

crystalline with characteristic peaks of vanadyl pyrophosphate phase and their surface morphologies were found to be in rosette-shape.

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