Vanadium(V) phosphate prepared using solvent-free method

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A solvent-free method of preparation of a vanadium(V) phosphate is described and discussed. Reaction of V_2O_5 with H_3PO_4 in the absence of water at 150 °C leads to the formation of a new catalytic material that is designated as "*anhydrous*" $VOPO_4$. The material readily hydrates to form $VOPO_4{\cdot}2H_2O$ and has been characterised using powder X-ray diffraction, *in situ* Raman spectroscopy and ^{31}P MAS NMR spectrometry. On activation in dry N_2 followed by reaction with butane/air another novel material is formed that has an intrinsic activity for maleic anhydride that is similar to catalysts derived from $VOHPO_4{\cdot}0.5H_2O$ under comparable conditions. Activation of $VOPO_4{\cdot}2H_2O$ under comparable conditions leads to the formation of α_I-$VOPO_4$ which exhibits no partial oxidation activity. Reaction of "*anhydrous*" $VOPO_4$ with alcohols leads to the exclusive formation of $VO(H_2PO_4)_2$ in further contrast to $VOPO_4{\cdot}2H_2O$ which under similar conditions leads to the synthesis of $VOHPO_4{\cdot}0.5H_2O$.

KEY WORDS: anhydrous $VOPO_4$; *n*-butane oxidation; maleic anhydride; $VOPO_4{\cdot}2H_2O$

1. Introduction

Vanadium phosphates have become one of the most studied heterogeneous catalytic systems and have been the subject of in excess of one thousand papers and patents [1–4] since their initial discovery by Bergmann and Frisch [5]. They are used commercially for the oxidation of *n*-butane to maleic anhydride [6] and experimental studies have shown that vanadium phosphates are also effective catalysts for propane [7] and pentane [8] partial oxidation. Most attention has focussed on the hemihydrate precursor phase, $VOHPO_4{\cdot}0.5H_2O$, which is transformed under reaction conditions to give a complex mixture of V(IV) and V(V) phases [9]. Although many preparation methods have been cited, virtually all are based on the reaction between a vanadium compound, typically V_2O_5, a phosphorus compound, typically H_3PO_4, and a reducing agent/solvent, typically an alcohol [10]. The alcohol is intercalated into the layer structure of the VPO compounds and the subsequent removal on heat treatment plays a central role in establishing the final surface area of the catalyst.

The alcohol also can play a role in establishing the morphology of the hemihydrate precursor, which, since the transformation to the final catalyst is topotactic, controls the morphology of the final catalyst. It is therefore clear that the solvent plays a valuable and identifiable function in the preparation of VPO materials. However, despite the large number of papers dealing with VPO catalyst preparation, the use of solvent-free conditions has not received attention. In a way, this lack of attention to solvent-free methods appears out of step with current environmental initiatives where the use of solvent-free reaction conditions has been identified as a major goal of the chemical industry for several years. We have now addressed the use of solvent-free preparation conditions. In this paper we communicate our initial results concerning the synthesis of a novel V(V) compound, designated anhydrous $VOPO_4$.

2. Experimental

2.1. Preparation of VPO compounds

2.1.1. Preparation of anhydrous $VOPO_4$

V_2O_5 (5.0 g, Strem) and H_3PO_4 (41.0 g, 100%, Aldrich) were heated in an autoclave at 150 °C for 16 h. The resultant yellow solid was slurried with acetone, recovered by filtration, washed with acetone (100 ml) and dried in air (110 °C, 16 h). The material was stored under desiccation.

2.1.2. Preparation of $VOPO_4{\cdot}2H_2O$

V_2O_5 (5.0 g, Strem) was refluxed with H_3PO_4 (30 ml, 85%, Aldrich) in water (120 ml) for 24 h. The yellow solid was recovered by vacuum filtration, washed with cold water (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h).

2.2. Partial oxidation of *n*-butane

The VPO compounds were evaluated for *n*-butane oxidation using a laboratory microreactor. Butane and air were premixed to give 1.5% butane in air and the gas flow was maintained using mass flow controllers. The reactor was a stainless-steel tube (i.d. 10 mm) with the VPO compounds held in place using quartz wool. Temperature control was achieved using a thermocouple inserted into the centre of the reactor tube and temperature control was generally ±1 °C. Gas lines to and from the reactor were constructed in stainless steel (3 mm) and were heated to prevent the conden-

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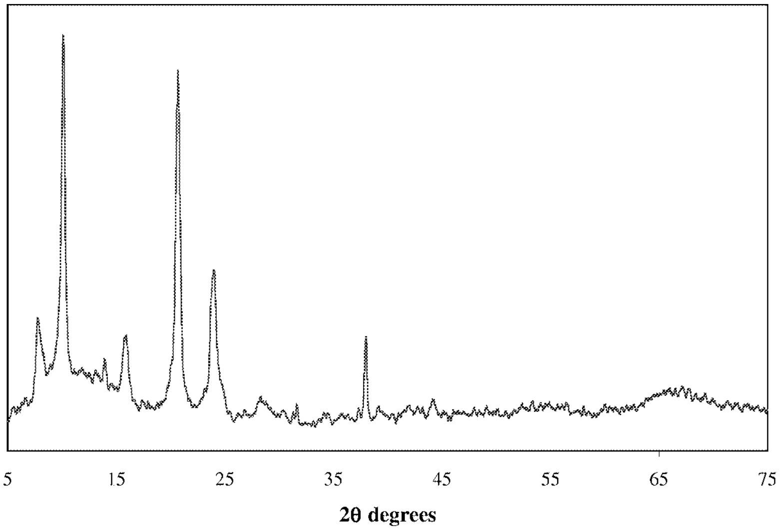


Figure 1. Powder X-ray diffraction pattern of material synthesised from the reaction of V_2O_5 with H_3PO_4 in the absence of solvent.

Table 1
Powder X-ray diffraction pattern of material prepared by the reaction of V_2O_5 with H_3PO_4.

Before activation[a]		After activation[b]	
d (Å)	I/I_0	d (Å)	I/I_0
11.173	32	4.192	97
8.644	100	3.957	43
6.324	22	3.863	100
5.518	27	3.449	27
4.261	94		
3.150	15		
2.818	13		
2.406	11		
2.364	33		
2.041	13		

[a] As synthesised.
[b] Activated by heating to 385 °C in dry N_2 and reaction with 1.5% n-butane in air for 24 h.

sation of maleic anhydride. Products were analysed using on-line gas chromatography.

2.3. Characterisation techniques

X-ray diffraction was performed using an Enraf Nonius FR 590 X-ray generator with a Cu K_α source fitted with an Inel CPS 120 hemispherical detector. BET surface area measurements were carried out using N_2 adsorption using a Micromeritics ASAP 2000 instrument. Raman spectra were obtained using a Renishaw Ramascope Spectrograph using a green Ar^+ laser ($\lambda = 514.532$ nm). ^{31}P MAS NMR spectroscopy was carried out using a Chemagnetics CMX-Infinity 400 MHz spectrometer.

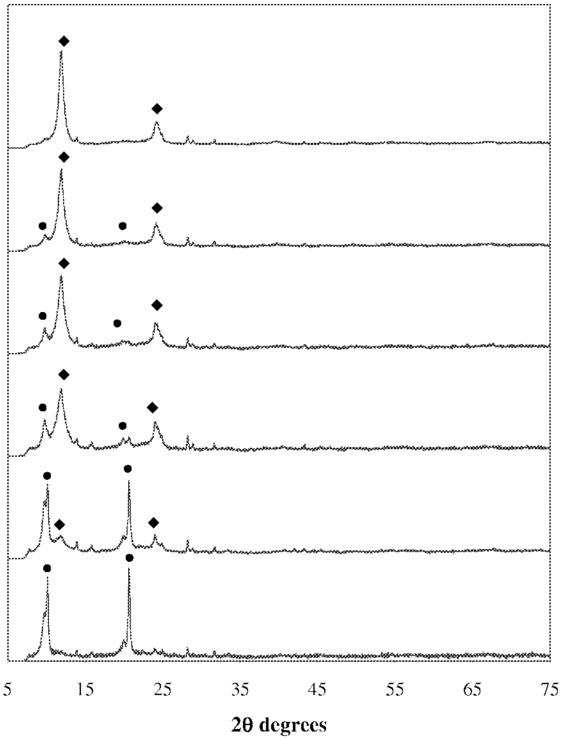


Figure 2. Powder X-ray diffraction pattern of the new material as a function of time: (●) reflexions of new material and (◆) reflexions of $VOPO_4 \cdot 2H_2O$.

3. Results

Reaction of V_2O_5 with H_3PO_4 in the absence of solvent (water or alcohol) results in the formation of a yellow crystalline solid with a powder X-ray diffraction pattern (figure 1, table 1) that does not correspond with any pattern previously reported for a vanadium phosphate. Some of the reflexions can be assigned to other $VOPO_4$ phases (e.g., $d = 3.150$ and 2.818 Å, $VOPO_4 \cdot 2H_2O$; $d = 4.261$ Å, α_{II}-$VOPO_4$), however, the intense [001] reflexion of $VOPO_4 \cdot 2H_2O$ at $d = 7.410$ Å is not observed. In particular the intense reflexions observed at $d = 11.173$ and 8.644 Å cannot be assigned to any known vanadium phosphate. It is therefore proposed that the material represents a new structure; however, it is found to be very air sensitive and this has hampered detailed electron microscopy and

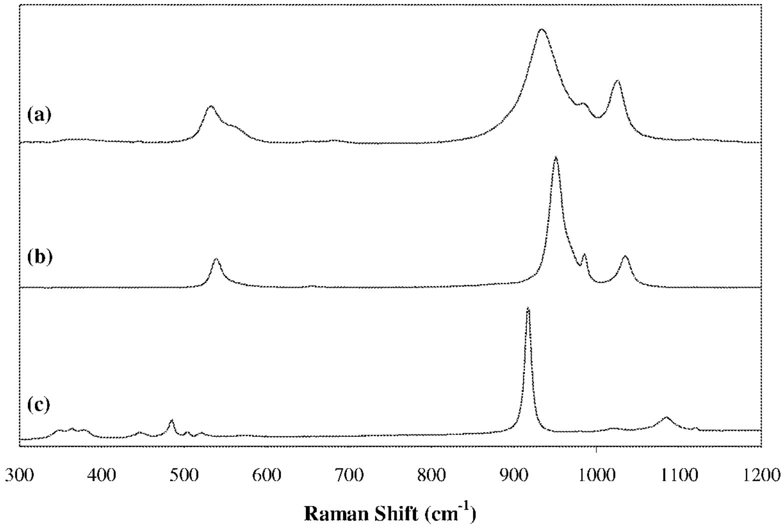


Figure 3. Laser Raman spectra of (a) new VPO material, (b) $VOPO_4{\cdot}2H_2O$ and (c) H_3PO_4.

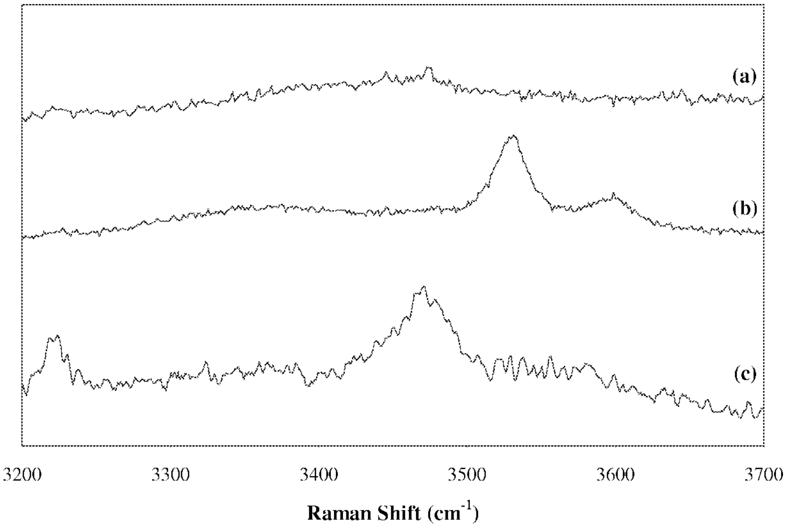
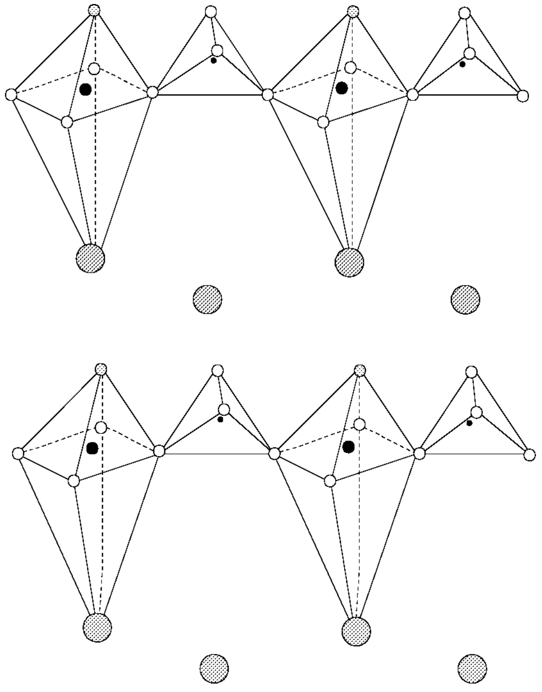


Figure 4. Laser Raman spectra of the hydroxyl region of (a) new VPO material, (b) $VOPO_4{\cdot}2H_2O$ and (c) H_3PO_4.

electron diffraction studies at this time. The material readily hydrates to $VOPO_4{\cdot}2H_2O$ and this hydration was followed using *in situ* powder X-ray diffraction (figure 2) for a sample of the new material exposed to air for 60 min. It is apparent that the intense reflexions at $d = 8.644$ and 4.261 Å decrease in intensity with increased air exposure and the powder X-ray diffraction pattern reverts to that of $VOPO_4{\cdot}2H_2O$.

Detailed Raman spectroscopy studies of the new VPO material have been carried out, and contrasted with the Raman spectra of $VOPO_2{\cdot}2H_2O$. The spectra are shown, together with that for H_3PO_4, in figure 3. The Raman spectra of the new material is very similar to that of $VOPO_2{\cdot}2H_2O$, but there are distinct differences in the Raman shift of the band positions.

The main Raman bands correspond to V=O, V–O–P and P–O stretches. The V=O bond lengths of all vanadium phosphates are known to be similar (1.57–1.58 Å), giving V=O stretch bands at 980–996 cm^{-1} [11], as observed by the bands at 986 cm^{-1} for $VOPO_4{\cdot}2H_2O$ and 985 cm^{-1} for the new material. The V–O–P stretch is related to the V–O–P bond angle: the larger the bond angle, the higher the frequency of the Raman band. In the new material this band is observed at 1026 cm^{-1} indicating that the bond angle is less than 133.7° as it is observed for $VOPO_4{\cdot}2H_2O$. In addition, there are new bands at 678, 554(sh) and 368 cm^{-1} for the new VPO material. The other intense band has been assigned to the $(PO_4)^{3-}$ symmetric stretch. This has shifted from 952 cm^{-1} in $VOPO_4{\cdot}2H_2O$ to 933 cm^{-1} in the new material. An additional key difference between the new VPO material and $VOPO_4{\cdot}2H_2O$ is observed in the OH stretch region of the Raman spectra (3200–3700 cm^{-1}, figure 4). For $VOPO_4{\cdot}2H_2O$, there are two weak, but distinct, Raman bands at 3530 and 3598 cm^{-1}. These are assigned to the OH stretches of the two crystallographically different water molecules in $VOPO_4{\cdot}2H_2O$ (figure 5). The band at 3530 cm^{-1} can be assigned to the water molecules bound to V^{5+} and the band at 3598 cm^{-1} can be assigned to the non-co-ordinated water. The new VPO material exhibits a broad,



[● = V, ▪ = P, o = vanadyl oxygen, ▒ = O,

▒ = H_2O free or co-ordinated to vanadium]

Figure 5. Structure of $VOPO_4 \cdot 2H_2O$.

and very weak, OH stretch centred at 3445 cm^{-1}. This is considered to be due to traces of water loosely associated with the structure, and is clearly distinct from the more intense bands for the OH stretches of the water of crystallisation in $VOPO_4 \cdot 2H_2O$ (figure 4). $VOPO_4 \cdot 2H_2O$ and H_3PO_4 also show weak, broad bands in this region of the spectrum.

The hydration of the new VPO material was investigated using *in situ* Raman spectroscopy in a similar manner to the *in situ* powder X-ray diffraction experiment. Water vapour was introduced to the VPO material as a 4 vol% in flowing argon. The results are shown in figure 6. The Raman spectrum of $VOPO_4 \cdot 2H_2O$ showed no changes in the presence of water vapour. However, for the new material the Raman bands dramatically decreased in intensity on introduction of water vapour. This loss of the Raman spectrum was unexpected, but the new VPO material is soluble in water and, consequently, we conclude that the water vapour is dissolving some of the surface of the crystallites and this leads to a loss of the focus of the laser beam.

The ^{31}P MAS NMR spectra of the new VPO material and $VOPO_4 \cdot 2H_2O$ were also contrasted (figure 7). There are clear differences in the ^{31}P NMR resonances of the two materials. The $VOPO_4 \cdot 2H_2O$ spectrum has a single resonance at 6.6 ppm confirming that all the phosphorus atoms are equivalent, whereas the new material has two resonances at 6.8 and 1.9 ppm. The shoulder at 0 ppm is due to unreacted H_3PO_4 being present in the sample.

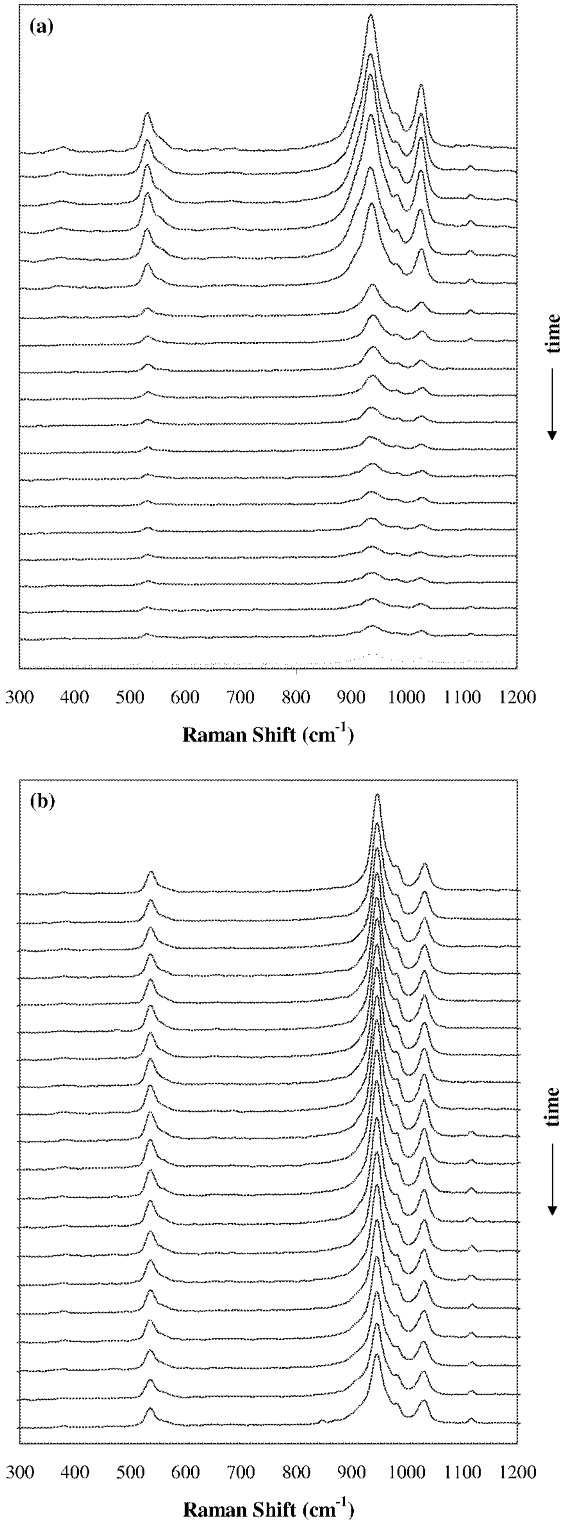


Figure 6. *In situ* laser Raman spectra of the effect of flowing H_2O/N_2 on (a) new VPO material and (b) $VOPO_4 \cdot 2H_2O$. Spectra taken at 5 min intervals.

The new material was investigated for *n*-butane oxidation at 385 °C. As the material was prone to rapid hydration the standard *in situ* pretreatment of the vanadium phosphate, in which the sample is heated in flowing 1.5% *n*-butane in air for 72 h [9], was not carried out. Instead, the sample was heated to 385 °C in dry N_2 and the flow of 1.5% n-butane in air was introduced when the reaction temperature was reached. The performance of the new material was compared with a standard sample of $VOPO_4{\cdot}2H_2O$ that had been treated in a similar manner (table 2). It is clear that the new material gives some selectivity to maleic anhydride whereas $VOPO_4{\cdot}2H_2O$ is totally non-selective giving mainly CO as product. The observed catalytic performance was unchanged (within ±1%) throughout a 24 h test period. Powder X-ray diffraction of the catalysts after the 24 h test period showed that the new material had transformed to a new phase, again characterised by two intense reflexions (figure 8, table 1). All these reflexions can be indexed to γ-$VOPO_4$, but the intense reflexions observed in literature samples of γ-$VOPO_4$ [12] are missing (e.g., $d = 4.897$ [013], 4.347 [032], 3.097 [105], 3.060 [311] and 2.453 Å [161]). This may indicate a preferred crystal morphology; however, the Raman spectrum of the material is not consistent with that of γ-$VOPO_4$ (figure 9). Clearly the final catalyst derived from the new material requires further characterisation. Analysis of the final catalyst derived from $VOPO_4{\cdot}2H_2O$ after 24 h catalyst testing showed that a different $VOPO_4$ phase was also formed; in this case the Raman spectrum (figure 10) was consistent with α_I-$VOPO_4$ [12].

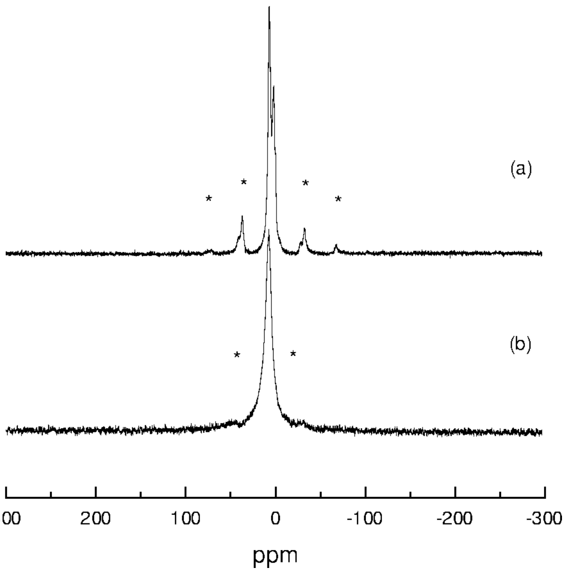


Figure 7. ^{31}P MAS NMR spectra (a) new VPO material and (b) $VOPO_4{\cdot}2H_2O$; $*$ denotes spinning side bands.

It is interesting to note that the reaction of n-butane with the new material at 385 °C is clearly more rapid than the reaction with water. The oxidation of n-butane with the new material as catalyst is not very selective and hence a high relative concentration of H_2O will also be present together with n-butane. However, the material is not hydrated to $VOPO_4{\cdot}2H_2O$, which is later transformed to α_I-$VOPO_4$ which is totally non-selective at these reaction conditions, but forms a material that may be related to γ-$VOPO_4$.

A further set of experiments were carried out to investigate the differences between the new material and

Table 2
Catalytic performance at 385 °C.[a]

Catalyst	Surface area (m^2)	Conversion (%)	Product selectivity (%)			Maleic anhydride intrinsic activity (10^6 mol m^{-2} h^{-1})
			Maleic anhydride	CO	CO_2	
$V_2O_5 + H_3PO_4$	3	11	16	60	24	11.5
$VOPO_4{\cdot}2H_2O$	0.2	21	0	93	7	0

[a] 1.5% n-butane in air, 385 °C, GHSV = 1000 h^{-1}.

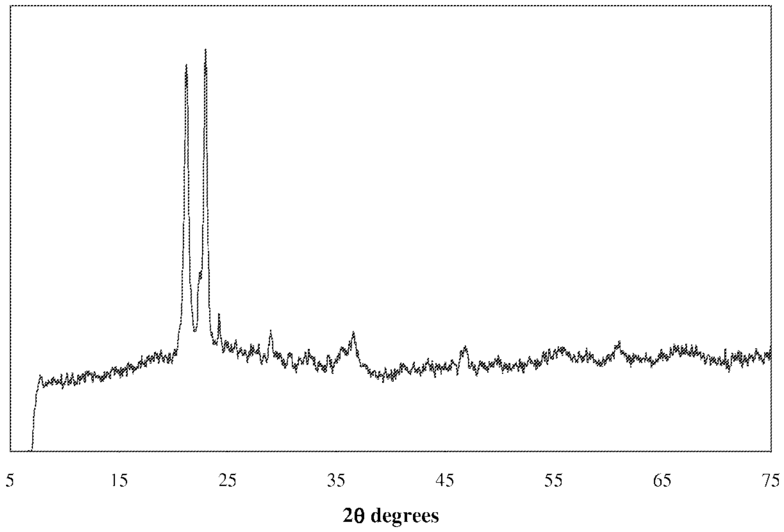


Figure 8. Powder X-ray diffraction pattern of new material after activation and n-butane oxidation.

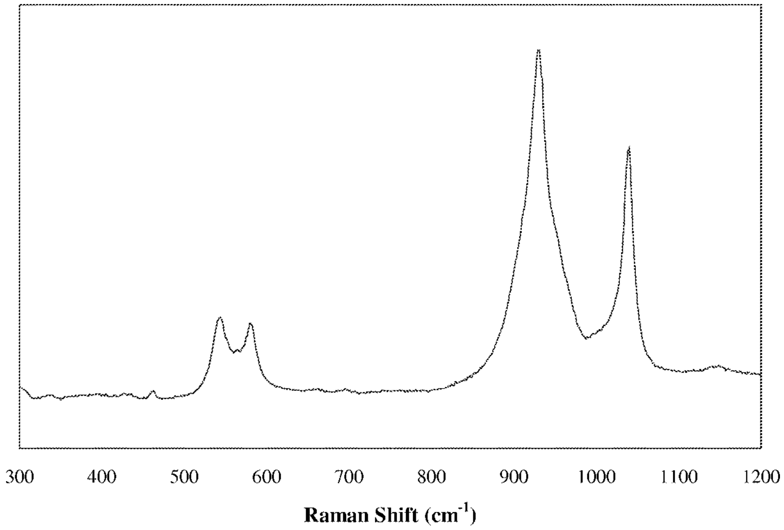


Figure 9. Laser Raman spectrum of new material after activation and *n*-butane oxidation.

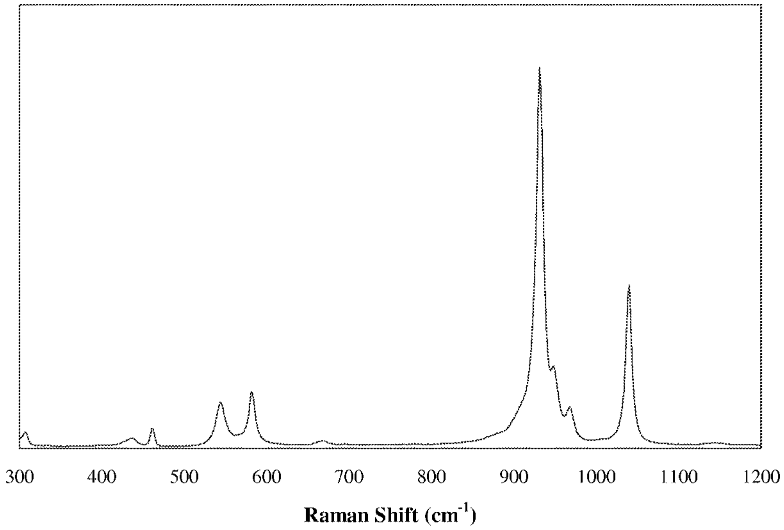


Figure 10. Laser Raman spectrum of $VOPO_4{\cdot}2H_2O$ after activation and *n*-butane oxidation.

$VOPO_4{\cdot}2H_2O$. Previous studies have shown [13,14] that $VOPO_4{\cdot}2H_2O$ can be readily reduced with a broad range of alcohols to form $VOHPO_4{\cdot}0.5H_2O$. In addition, the choice of alcohols is known to control the morphology of the $VOHPO_4.0.5H_2O$ crystallites [13]. The new material was refluxed with a range of alcohols (50 mol alcohol/mol V) for 16 h. In all cases $VO(H_2PO_4)_2$ was the observed product as determined by powder X-ray diffraction (figure 11) and laser Raman spectroscopy, and the choice of alcohol did not effect the morphology of the $VO(H_2PO_4)_2$ crystallites.

4. Discussion

It is clear that the reaction of V_2O_5 and H_3PO_4 in the absence of solvent leads to the formation of a new material that can readily be hydrated to $VOPO_4{\cdot}2H_2O$. Ben Abdelouahab et al. [15] have previously shown that, with the exception of β-$VOPO_4$, which is not a layer structure, all $VOPO_4$ phases hydrate to form $VOPO_4{\cdot}2H_2O$. Using air saturated with water vapour, the changes in the structure were monitored using laser Raman spectroscopy. The different phases were found to exhibit different stabilities: α_{II}-$VOPO_4$ required 10 h for hydration, γ-$VOPO_4$ and δ-$VOPO_4$ required 3 h and α_I-$VOPO_4$ only 45 min for hydration to $VOPO_4{\cdot}2H_2O$. This leads us to conclude that the new material is a $VOPO_4$ layer structure comprising of VO_6 octahedra and PO_4 tetrahedra. This suggestion is supported by powder X-ray diffraction data. The [001] reflexion in the powder X-ray diffraction patterns of $VOPO_4{\cdot}2H_2O$, $VOPO_4{\cdot}H_2O$ and α_I-$VOPO_4$ is an indication of the layer spacing, and this decreases from 7.45 Å in $VOPO_4{\cdot}2H_2O$, 6.37 Å in $VOPO_4{\cdot}H_2O$ to 4.11 Å in α_I-$VOPO_4$. The diffraction reflexion at $d = 8.644$ Å in the new material would indicate a very large inter-layer distance which would facilitate hydration.

The two resonances in the ^{31}P NMR of the new material suggests that, as in γ- and δ-$VOPO_4$, there are two different phosphorus environments present. However, the Raman

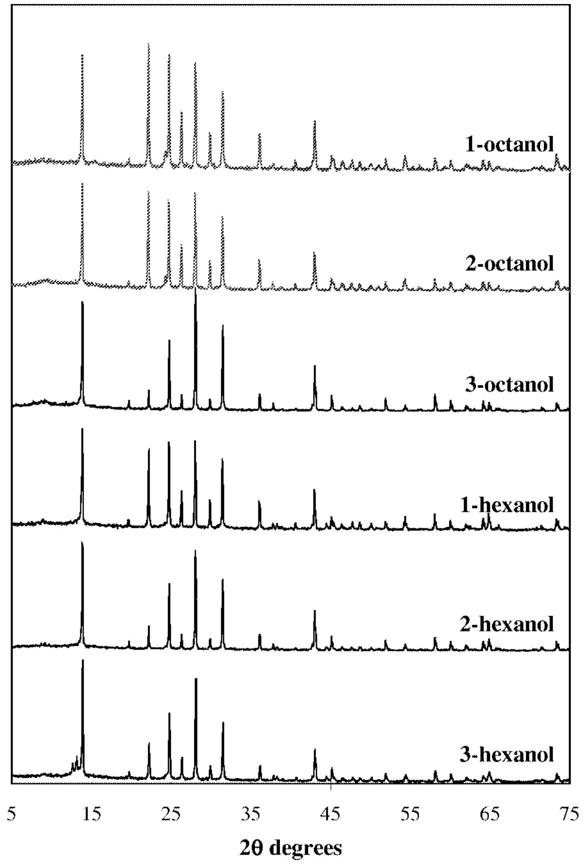


Figure 11. Powder X-ray diffraction patterns of $VO(H_2PO_4)_2$ prepared from the reaction of the novel material with alcohols. Main reflexions indexed to $VO(H_2PO_4)_2$.

spectrum only has one band associated with $(PO_4)^{3-}$. Alternatively there may be co-ordinated H_3PO_4 present in the new material. This would explain the downfield shift of the resonances compared to the pure $VOPO_4$ phases, and would also account for the large d-spacing observed in the powder XRD pattern. Further evidence for this proposal was obtained by exposing γ-$VOPO_4$ to H_3PO_4; the resulting spectrum contained the two expected resonances at -17 and -21 ppm, characteristic of γ-$VOPO_4$ [11], together with a strong resonance at 2 ppm with strong associated spinning side bands, indicating the presence of strongly coordinated H_3PO_4. Hence, it is proposed that the new material consists of structural phosphorus nuclei similar in environment to those of $VOPO_4{\cdot}2H_2O$, coordinated to which are strongly adsorbed H_3PO_4. Although further detailed investigation is required, we suggest that the new material formed in the absence of solvent is “*anhydrous*” $VOPO_4$.

The use of solvent-free preparation methods of vanadium phosphate synthesis could lead to a new and fruitful area of investigation. Many previous investigations have used novel methodology, in place of the well established routes based on V_2O_5 reacting with H_3PO_4 in a reducing solvent, but all have led to the formation of activated catalysts containing $(VO)_2P_2O_7$. For example, Bordes and Courtine [16] prepared a number of precursors based on $NH_4(VO_2)_2PO_4$, $(NH_4)_2[(VO_2)_2C_2O_4(H_3PO_4)_2]{\cdot}5H_2O$ and NH_4HVPO_6 which all lead to the formation of $(VO)_2P_2O_7$ together with $VO(PO_3)_2$ or $V(PO_3)_2$. Benziger et al. [17] synthesised vanadyl phosphonates ($VOC_nH_{2n+1}PO_3{\cdot}xH_2O$; $n = 0$–4, $x = 1$ or 1.5) which on activation led to the formation of $(VO)_2P_2O_7$. Interestingly, in this study, the use of solvent-free conditions has led to the formation of a new material that does not transform to $(VO)_2P_2O_7$ or $VO(PO_3)_2$ on activation. Although the new material has low selectivity to maleic anhydride, the intrinsic activity for maleic anhydride formation is very similar to that for catalysts comprising of $(VO)_2P_2O_7$, together with α_{II}-, δ- or γ-$VOPO_4$, reported in our previous studies [14,18], in the range (5–12) $\times 10^{-6}$ mol maleic anhydride/m^2 h. This suggests that the material is worthy of further investigation for hydrocarbon partial oxidation.

Acknowledgement

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