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n-Butane oxidation using $VO(H_2PO_4)_2$ as catalyst derived from an aldehyde/ketone based preparation method

Jonathan K. Bartley,[a] Colin Rhodes,[a] Christopher J. Kiely,[b] Albert F. Carley[a] and Graham J. Hutchings*[b]

[a] *Department of Chemistry, Cardiff University, Cardiff, UK CF10 3TB*
[b] *Department of Chemistry and Department of Material Science and Engineering, University of Liverpool, UK L69 3BX*

Received 30th March 2000, Accepted 29th June 2000
First published as an Advance Article on the web 29th September 2000

A detailed study of *n*-butane oxidation over vanadium phosphate catalysts derived from *in situ* activation of $VO(H_2PO_4)_2$ is described and discussed. New methods of preparation of $VO(H_2PO_4)_2$ are described using the reaction of V_2O_5 and H_3PO_4 or $VOPO_4 \cdot 2H_2O$ with an aldehyde or ketone as a reducing agent. It is proposed that the enol form of the aldehyde and ketone act as the reducing agent. $VO(H_2PO_4)_2$ can also be obtained by reduction of $VOPO_4$ phases with alcohols. The catalysts derived from $VO(H_2PO_4)_2$ by *in situ* activation in 1.5% butane in air at 400 °C for 72 h are largely disordered and, by detailed powder X-ray diffraction and laser Raman spectroscopy, are shown to be comprised mainly of disordered material containing some untransformed $VO(H_2PO_4)_2$, $VOPO_4$ phases and possibly some $VO(PO_3)_2$. The catalysts derived from all the forms of $VO(H_2PO_4)_2$ investigated are found to exhibit maleic anhydride selectivities in the range 20–30% and it is concluded that the low selectivity is due to the presence of $VOPO_4$ phases in the activated catalysts.

Introduction

Vanadium phosphate compounds are utilised commercially as catalysts for the synthesis of maleic anhydride from the partial oxidation of *n*-butane. As a result, vanadium phosphates have been extensively studied,[1–4] however, most attention has focused on the synthesis of suitable catalytic materials. The current preferred catalyst is derived from *in situ* activation,[5] under reaction conditions, of $VOHPO_4 \cdot 0.5H_2O$.[6,7] The activated catalyst comprises a complex mixture of $(VO)_2P_2O_7$ in combination with α_{II}- and δ-$VOPO_4$ phases.[6] Some researchers[8] favour $(VO)_2P_2O_7$ as the sole active phase, based primarily on powder X-ray diffraction data, and have concluded that the presence of other vanadium phosphates is due to incomplete activation. However, *in situ* Raman spectroscopy suggests that specific combinations of V^{4+} and V^{5+} phases are a necessary requirement for the catalyst to exhibit high activity and selectivity to maleic anhydride simultaneously. Recently, Coulston *et al.*[9] have shown that the presence of V^{5+} appears to be essential for the initial activation of *n*-butane, an observation that is consistent with observations using a TAP (temporal analysis of products) pulse reactor.[10] The debate concerning the importance of specific crystalline phases of vanadium phosphates is complicated by the observation of 'disordered material' or 'partly crystalline $(VO)_2P_2O_7$' in vanadium phosphate catalysts prepared in organic media.[11] These disordered materials are likely to exhibit V^{5+} and V^{4+} ions in close proximity. In view of the emphasis on catalysts derived from $VOHPO_4 \cdot 0.5H_2O$, few alternative catalyst precursors have been investigated. To some extent this is due to the fact that $VOHPO_4 \cdot 0.5H_2O$ is easily prepared by a range of methods and readily crystallises from solutions containing $(VO)^{2+}$ and H_3PO_4 in the presence of aqueous HCl[4,5] or organic reducing agents, typically alcohols.[7,11,12] A preferred method of preparation involves refluxing V_2O_5 in a solution of H_3PO_4 in an alcohol for *ca.* 16 h, and this produces very pure samples of $VOHPO_4 \cdot 0.5H_2O$.[12] In this preparation procedure the alcohol is oxidised to form either an aldehyde or a ketone. This has prompted us to consider the role of aldehydes and ketones in the preparation method, and in this paper we investigate vanadium phosphate catalysts prepared using aldehydes and ketones in place of alcohols. Interestingly, we have found that replacement of the alcohol by an aldehyde or ketone leads to the formation of $VO(H_2PO_4)_2$. This water-soluble vanadium phosphate has been shown to be present in low quantities in many samples of $VOHPO_4 \cdot 0.5H_2O$[4,13] and has been implicated in the poor catalyst performance of these materials.[13] More recently, a sample of $VO(H_2PO_4)_2$ prepared by treatment of $VOPO_4 \cdot 2H_2O$ with octan-3-ol[14] was found to be highly selective when tested in a differential reactor.[15–17] In this paper, we investigate the catalytic performance of $VO(H_2PO_4)_2$ prepared by a range of methods.

Experimental

Catalyst preparation

Preparation of $VOPO_4 \cdot 2H_2O$.[17] V_2O_5 (5.0 g Strem.) was refluxed with H_3PO_4 (30 ml, 85% Aldrich) (P/V molar ratio = 15) in water (120 ml) for 24 h. The yellow solid (yield 50% based on V) was recovered by vacuum filtration, washed with cold water (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h).

Preparation of β$VOPO_4$.[18] $NH_4(VO)_2PO_4$ (1 g, prepared according to the method of Bordes and Courtine[19]) was oxidised in flowing dry air (50 ml min^{-1}). The temperature was increased from ambient at a rate of 1 °C min^{-1} to 600 °C and then maintained at this temperature for 10 h.

Preparation of γ$VOPO_4$.[18] $VOHPO_4 \cdot 0.5H_2O$ (1 g, prepared according to the method of Kiely *et al.*[6]) was heated in flowing dry oxygen (50 ml min^{-1}). The temperature was

DOI: 10.1039/b002553o

increased from ambient at a rate of 2 °C min^{-1} to 680 °C and maintained at this temperature for 4 h.

Preparation of $\delta VOPO_4$.[18] $VOHPO_4 \cdot 0.5H_2O$ (1 g) was heated in flowing dry oxygen (50 ml min^{-1}). The temperature was increased from ambient at a rate of 1 °C min^{-1} to 680 °C and maintained at this temperature for 168 h.

Preparation of "*anhydrous*" $VOPO_4$. An unidentified crystalline V^{5+} vanadium phosphate (designated "*anhydrous* $VOPO_4$") was prepared by heating V_2O_5 (5.0 g, Strem) and H_3PO_4 (41.0 g, 100%, Aldrich) (P/V molar ratio = 15) 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, on treatment with moist air $VOPO_4 \cdot 2H_2O$ formed and it is for this reason that the material has been designated "*anhydrous* $VOPO_4$."

Preparation of $VO(H_2PO_4)_2$. (*a*) *From* $VOPO_4 \cdot 2H_2O$. $VOPO_4 \cdot 2H_2O$ (4 g) was refluxed with octan-3-ol (50 (mol alcohol) (mol $VOPO_4 \cdot 2H_2O)^{-1}$, Aldrich) for 16 h. The resultant pale blue solid was recovered by vacuum filtration, washed with octan-3-ol (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h).

(b) *From "anhydrous* $VOPO_4$". Anhydrous $VOPO_4$ (2 g) was refluxed with an alcohol (80 ml, Aldrich) for 16 h. The resultant solid was recovered by vacuum filtration, washed with the alcohol (50 ml) and acetone (50 ml) and dried in air (110 °C, 16 h).

(c) *Using aldehydes and ketones.* (i) VPO method:[6] V_2O_5 (1.0 g. Strem), H_3PO_4 (2.8 g, 85%, Aldrich) (P/V molar ratio = 4.5) and an aldehyde/ketone (40 ml, Aldrich) were refluxed for 16 h. The resultant pale blue solid (yield 85.95% based on V) was recovered by vacuum filtration, washed with the aldehyde/ketone (50 ml) and acetone (50 ml) and dried in air (110 °C, 24 h). (ii) VPD method:[6] $VOPO_4 \cdot 2H_2O$ (1.0 g), H_3PO_4 (0.05 g, 85%, Aldrich) (mole ratio $VOPO_4 \cdot 2H_2O : H_3PO_4 = 8 : 1$) and the aldehyde/ketone (40 ml, Aldrich) were refluxed for 16 h. The solid was recovered by vacuum filtration, washed with the aldehyde/ketone (50 ml) and acetone (50 ml) and dried in air (110 °C, 24 h).

(d) *Using excess* H_3PO_4. (i) VPO method:[6] V_2O_5 (1.0 g, Strem) and H_3PO_4 (10.0 g, 85%, Aldrich) (P/V molar ratio = 15) and the alcohol (40 ml, Aldrich) were refluxed for 16 h. The solid (yield 85.95% based on V) was recovered by vacuum filtration, washed with the alcohol (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h). (ii) VPD method:[4] $VOPO_4 \cdot 2H_2O$ (1.0 g), H_3PO_4 (10.0 g, 85%, Aldrich) and the alcohol (40 ml, Aldrich) were refluxed for 16 h. The solid (yield 40–45% based on V) was recovered by vacuum filtration, washed with the alcohol (50 ml) and acetone (50 ml) and dried in air (110 °C, 24 h).

(e) *Reduction of* $VOPO_4$ *phases.* $VOPO_4$ was refluxed in isobutanol (40 ml, Aldrich) for 16 h. The solid was recovered by vacuum filtration, washed with isobutanol (50 ml) and acetone (50 ml) and dried in air (110 °C, 16 h).

All samples were stored in sealed containers under desiccation prior to their investigation as catalysts, for which the materials were pelleted and sieved to give particles (diameter: 200–300 μm).

Catalyst testing and characterisation

The oxidaton of *n*-butane was carried out using a microreactor using a standard volume of catalyst (0.5 ml). *n*-Butane and air were fed to the reactor *via* calibrated mass flow controllers to give a feedstock composition of 1.5% *n*-butane in air. The products were fed *via* heated lines to an on-line gas chromatograph for product 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 °C. Carbon mass balances of $\geqslant 95\%$ were typically observed. $VO(H_2PO_4)$ catalyst precursors were activated *in situ* (1.5% *n*-butane in air, 1000 h^{-1}) at 400 °C for 72 h.

A number of physical techniques were employed to characterise the catalyst microstructure. Powder X-ray diffraction (XRD) was performed using an Enraf Nonius FR590 X-ray generator with a Cu-Kα source fitted with an Inel CPS 120 hemispherical detector. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics ASAP 2000 instrument. Raman spectra were obtained using a Renishaw Ramanscope Spectrograph fitted with a green Ar^+ laser ($\lambda = 514.532$ nm). Transmission electron microscopy (TEM) analysis was carried out as described previously.[6]

X-ray photoelectron spectroscopy (XPS) was used to determine the P/V surface atomic ratio. XPS measurements were made using a VG ESCA3 photoelectron spectrometer employing an Al-Kα X-ray source operating at 400 W. Samples were mounted using double-sided adhesive tape. Binding energies were referenced to the C(1s) peak at 285 eV and P : V ratios calculated using the relative sensitivity factors due to Wagner.[19]

Results and discussion

Catalyst precursor characterisation

Aldehydes and ketones as reducing agents. The VPO preparation method[6] was investigated using aldehydes and ketones in place of the alcohol.[6,12] Surprisingly, this method of precursor preparation led exclusively to the formation of $VO(H_2PO_4)_2$ and the XRD patterns and laser Raman spectra are shown for a range of carbonyl compounds in Fig. 1 and 2. Previously,[14–17] $VO(H_2PO_4)_2$ had only been formed exclusively in VPD-type preparations[6] with $VOPO_4 \cdot 2H_2O$ using octan-3-ol as the reducing agent, and the XRD pattern obtained for $VO(H_2PO_4)_2$ from the aldehydes and ketones was identical with that prepared from $VOPO_4 \cdot 2H_2O$ with octan-3-ol[14–17] or previously reported by Bordes.[2] In addition, the Raman spectra were very similar to that observed previously by Guliants *et al.*[20] (1151 cm^{-1}, br, m; 935 cm^{-1}, vs; 900 cm^{-1}, sh, m; 575 cm^{-1}, m). Scanning electron microscopy (SEM) and TEM micrographs for $VO(H_2PO_4)_2$ prepared using aldehydes and ketones are contrasted with those from $VO(H_2PO_4)_2$ prepared from $VOPO_4 \cdot 2H_2O$ with octan-3-ol and are shown in Fig. 3 and 4. The material prepared from octan-3-ol has a blocky morphology with regular sided oblong crystallites with the ratio of the sides being 1 : 1 : 2 regardless of the dimensions of the crystal.[17] However, it is clear that the crystallites are not single crystal faces since the surfaces are marked with many indentations (Fig. 4(a)). In contrast, $VO(H_2PO_4)_2$ prepared using aldehydes and ketones as reducing agents has needle-shaped crystals which, at higher magnification, do not reveal the presence of surface indentations (Fig. 4(b)). Hence, the solvent used to prepare $VO(H_2PO_4)_2$ can control the morphology of the crystallites. This is similar to the effects observed for alcohols in the preparation of $VOHPO_4 \cdot 0.5H_2O$.[14]

Apart from the sample produced using butan-2-one, all samples of $VO(H_2PO_4)$ prepared using aldehydes and ketones were well crystalline and all diffraction and spectral features could be ascribed to $VO(H_2PO_4)_2$. For butan-2-one, two additional weak diffraction lines with *d*-spacings 6.992 and 6.727 Å were observed, but these cannot be indexed with other vanadium phosphate phases. It is, therefore, considered that this preparation method represents a novel route to high quality $VO(H_2PO_4)_2$. In addition, it is a general method of preparation since $VO(H_2PO_4)_2$ can be produced from the reaction of V_2O_5 and H_3PO_4 with all aldehydes and ketones

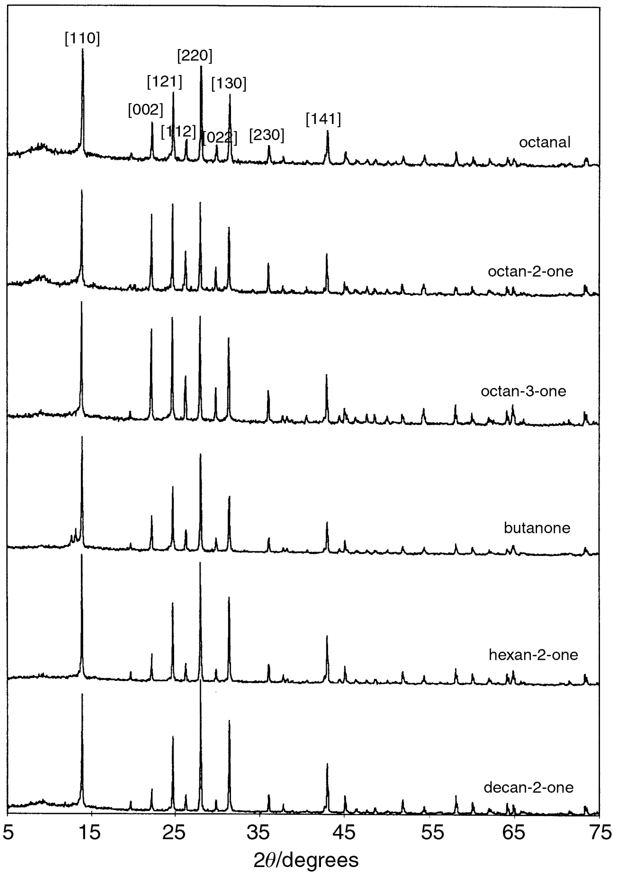


Fig. 1 Powder XRD patterns of VPO precursors prepared using aldehydes and ketones as reducing agents. The pattern is indexed to the reflexions for $VO(H_2PO_4)_2$.

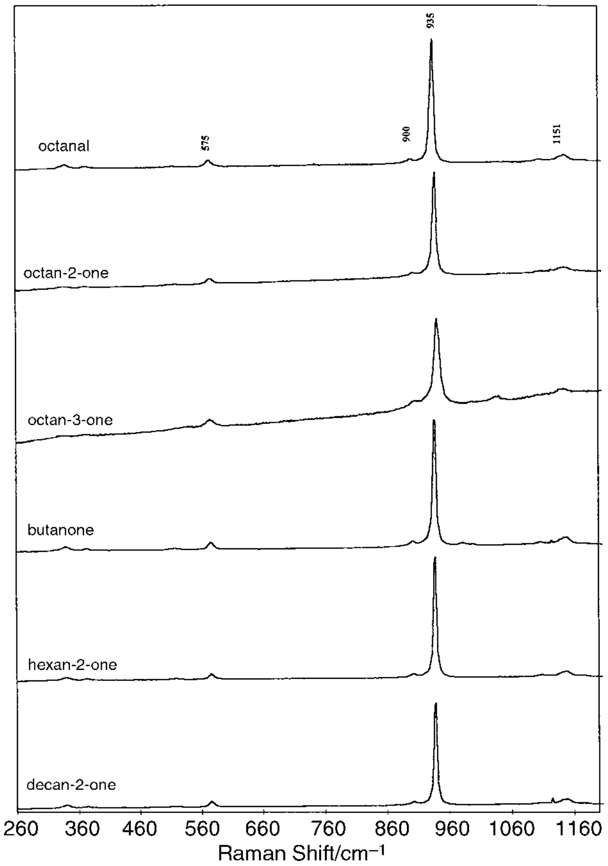


Fig. 2 Raman spectra of VPO precursors prepared using aldehydes and ketones as reducing agents.

in the range C_4–C_{10} investigated to date and only representative data are given in the figures.

The VPD preparation method[6] was also investigated with aldehydes and ketones but, in the absence of an acid, $VOPO_4 \cdot 2H_2O$ was not reduced by aldehydes and ketones. However, on addition of H_3PO_4 ($VOPO_4 \cdot 2H_2O : H_3PO_4 = 1 : 0.1$ molar ratio), the reduction reaction was observed and, again, $VO(H_2PO_4)_2$ was obtained as the exclusive product for all aldehydes and ketones examined in the range C_4–C_{12}. Representative data of $VO(H_2PO_4)_2$ prepared for the C_8 series are shown in Fig. 5 and 6 and all the diffraction and spectral data are consistent with the formation of $VO(H_2PO_4)_2$.

$VO(H_2PO_4)_2$ prepared using excess H_3PO_4. Early reports of the preparation of $VO(H_2PO_4)_2$ by Ladwig[21] indicated that the material was synthesised from the reaction of V_2O_5 and excess H_3PO_4 in aqueous HCl. The reaction of V_2O_5 with a stoichiometric quantity of H_3PO_4 in aqueous HCl is well known[4] to produce $VOHPO_4 \cdot 0.5H_2O$, and $VO(H_2PO_4)_2$ is a known impurity formed by this preparation method.[13] Although the reaction of V_2O_5 and H_3PO_4 in an alcohol, VPO preparation method[6,12,17] or $VOPO_4 \cdot 2H_2O$ with alcohols, VPD preparation method,[6,17] has been well studied, the addition of excess H_3PO_4 in this preparation route has not been explored. The addition of excess H_3PO_4 in the VPO and VPD preparation methods again led exclusively to the formation of $VO(H_2PO_4)_2$. The XRD patterns, Raman spectra and TEM analysis showed these materials to be identical to the material prepared from the reduction of $VOPO_4 \cdot 2H_2O$ with octan-3-ol[17] (Fig. 4(a)). In the preparation of $VOHPO_4 \cdot 0.5H_2O$ from the reduction of $VOPO_4 \cdot 2H_2O$, the nature of the alcohol significantly affected the morphology of the crystals formed.[14] However, the preparation of $VO(H_2PO_4)_2$ from $VOPO_4 \cdot 2H_2O$ showed no effect of the alcohol on crystal morphology and all materials were identical.

$VO(H_2PO_4)_2$ prepared from $VOPO_4$. Reduction of the synthesised "*anhydrous* $VOPO_4$" with a range of alcohols (C_4–C_8) was found to provide an additional preparation method for the synthesis of $VO(H_2PO_4)_2$. The powder XRD patterns, as shown in Fig. 7 for hexan-1-,2-,3-ol and octan-1-, 2-,3-ol as representative examples, and no additional vanadium phosphates are present in the samples. In addition, it is apparent that the alcohol has no effect on the morphology of the $VO(H_2PO_4)_2$ crystallites.

As the "*anhydrous* $VOPO_4$" hydrates to $VOPO_4 \cdot 2H_2O$ on exposure to moist air, it was decided to investigate the effect of alcohol reduction on β-, γ- and δ-$VOPO_4$. Reduction of β- and δ-$VOPO_4$ with isobutanol did not result in the formation of $VO(H_2PO_4)_2$. Reduction of γ-$VOPO_4$ with isobutanol did form $VO(H_2PO_4)_2$ but together with a significant amount of $VOHPO_4 \cdot 0.5H_2O$ (Fig. 8). These experiments show that the method based on "*anhydrous* $VOPO_4$" provides a facile route to pure $VO(H_2PO_4)_2$ that is not achievable from the other $VOPO_4$ phases.

n-Butane oxidation studies and post-reaction characterisation

$VO(H_2PO_4)_2$ samples prepared according to the range of methods detailed in this paper, were used as catalyst precursors for the oxidation of *n*-butane. The catalysts were activated *in situ* in the reactor with flowing *n*-butane (1.5%) in air at 385–415 °C for 72 h. During this time, the conversion of *n*-butane gradually increased, but between 72–300 h reaction time the catalytic performance was unchanged and the results for the activated catalysts are given in Table 1, with a fresh catalyst precursor being used for each condition evaluated. The catalysts derived from $VO(H_2PO_4)_2$ gave similar results

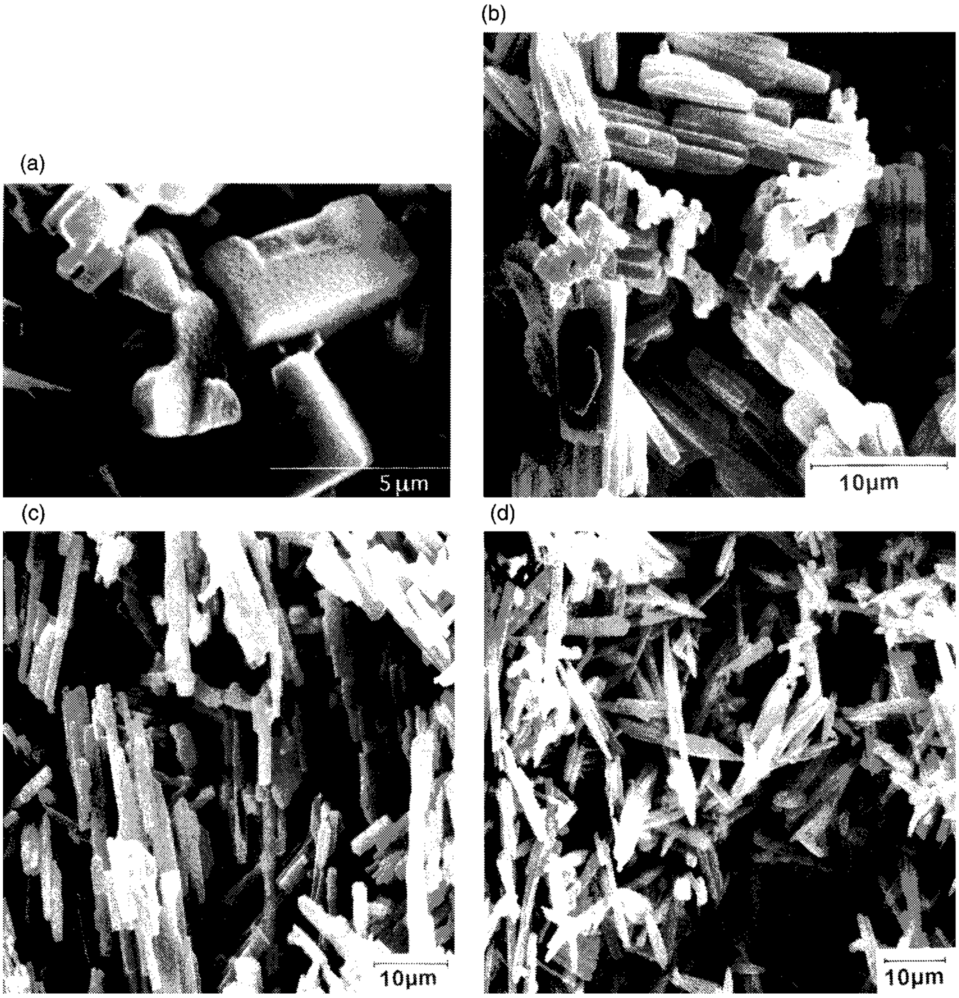


Fig. 3 SEM micrographs of $VO(H_2PO_4)_2$. (a) $VOPO_4 \cdot 2H_2O$ and octan-3-ol, (b) VPO method with octanal, (c) VPO method with octan-2-one, (d) VPO method with octan-3-one.

and no dependence on the preparation route was apparent. The surface area of all activated catalysts was found to be in the range 1–3 $m^2\ g^{-1}$ and this is similar to that observed previously,[17] and the specific activity ((mol maleic anhydride) $m^{-2}\ h^{-1}$) is similar to that reported in the previous study. The maleic anhydride selectivity observed with these catalysts is typically 20–30%, even at low conversion levels, and the primary selectivity S_0 (obtained by extrapolating the maleic anhydride selectivity to zero *n*-butane conversion, the conversion being varied by changing the flow rate at constant temperature) for all the samples, is 30 ± 5%. This is in contrast to our earlier study which indicated that no carbon oxides were formed with a catalyst derived from $VO(H_2PO_4)_2$ using a differential reactor with a powdered catalyst.[16,17] Although it is possible that the different reaction testing conditions may contribute to the significantly lower selectivity, it should be noted that the present study is very detailed and involves the investigation of a wide range of $VO(H_2PO_4)_2$ samples prepared by a number of different methods. The cata-

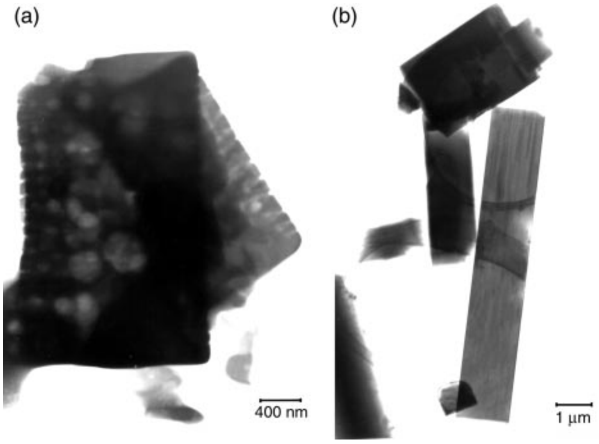


Fig. 4 Bright field transmission electron micrographs for $VO(H_2PO_4)_2$. (a) $VOPO_4 \cdot 2H_2O$ and octan-3-ol, (b) VPO method with octan-2-one.

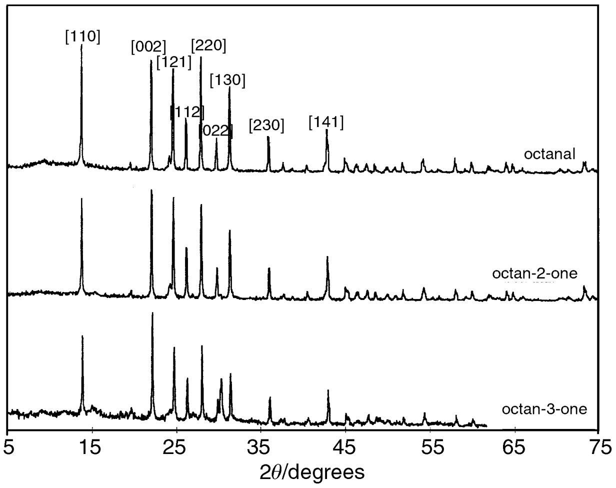


Fig. 5 Powder XRD patterns of VPD precursors prepared using octanal, octan-2-one and octan-3-one.

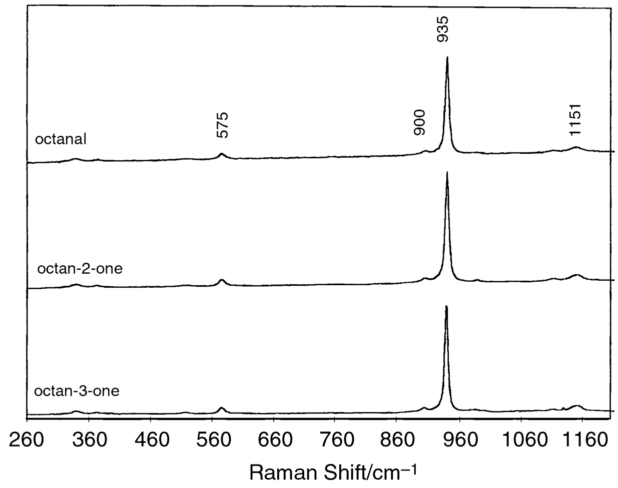


Fig. 6 The Raman spectra of VPD precursors prepared using aldehydes and ketones as reducing agents.

lytic performance is in agreement with a number of previous studies in which $VO(H_2PO_4)_2$ has been used as a precursor. Mount and Raffelson[22] studied $VO(H_2PO_4)_2$ as a catalyst precursor prepared by heating V_2O_5 and H_3PO_3 in an autoclave at 150 °C. Hannour *et al.*[23] prepared $VO(H_2PO_4)_2$ by heating an aqueous solution of V_2O_5, H_3PO_4 and oxalic acid. Hutchings and Higgins[13] showed that $VO(H_2PO_4)_2$ could be obtained from vanadium phosphate catalysts by water extraction. In all these cases, the catalyst obtained from *in situ* activation of $VO(H_2PO_4)_2$ gave very low selectivities to maleic anhydride.

The catalyst structures were examined following reaction using powder XRD (Fig. 9) and Raman spectroscopy (Fig. 10). The XRD patterns show a varying degree of crystallinity. Most patterns comprise three lines which have been observed previously[16,17] and these have been assigned in those studies to $VO(PO_3)_2$. However, these peaks cannot be definitively assigned to a specific vanadium phosphate. All three diffraction lines can be indexed to $VO(H_2PO_4)_2$ which may indicate that the catalysts are mainly disordered and contain non-transformed $VO(H_2PO_4)_2$ in variable amounts. The diffraction lines at *ca.* 23° and 29° can also be indexed to the [220] and [211] reflexions of $VO(PO_3)_2$, which can be formed from $VO(H_2PO_4)_2$ by heat treatment.[3,21,22] Raman spectra help clarify the assignment. The Raman spectra of catalysts have a strong broad band with a Raman shift of 935 cm^{-1}, which is characteristic of $VO(H_2PO_4)_2$.[20] Gulients *et al.* have shown that the Raman spectra of $VO(PO_3)_2$ has a strong band with a Raman shift of 957 cm^{-1}. None of the spectra (Fig. 10) show a pronounced band at 957 cm^{-1} although most show a broadening of the 935 cm^{-1} band in this spectral region. However, other bands for $VO(H_2PO_4)_2$ (575, 900, 1151 cm^{-1}) and $VO(PO_3)_2$ (692, 1065 and 1109 cm^{-1}) are absent from these spectra. There are a number of bands in the 950–1150 cm^{-1} region which may be due to $VOPO_4$ phases[5] which are commonly found in catalysts derived from $VOHPO_4 \cdot 0.5H_2O$ (V=O stretch: 1091 cm^{-1}, α_{II}-$VOPO_4$; 1040 and 1096 cm^{-1}, γ-$VOPO_4$; 1010 cm^{-1}, δ-$VOPO_4$).

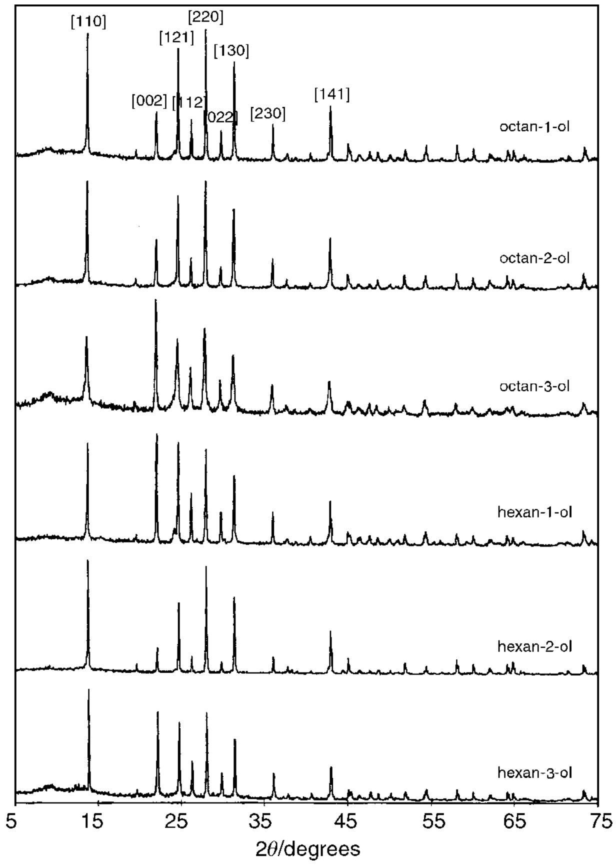


Fig. 7 Powder XRD patterns for $VO(H_2PO_4)_2$ prepared by alcohol reduction of "*anhydrous* $VOPO_4$".

Table 1 *n*-Butane oxidation over catalysts derived from $VO(H_2PO_4)_2$

Preparation Method	Temperature /°C	Surface area final catalyst /m^2 g^{-1}	*n*-Butane conversion (%)	Selectivity (%) MA	CO	CO_2	Specific activity 10^{-5} mol m^{-2} h^{-1}
$VOPO_4 \cdot 2H_2$/octan-3-ol	385	0.9	18.5	21	50	29	1.15
$VOPO_4 \cdot 2H_2$/octan-3-ol	400	2.2	21.8	20	53	27	1.27
$VOPO_4 \cdot 2H_2$/octan-3-ol	415	2.2	24.7	18	55	27	1.34
VPO/octanol	385	1.2	16.6	27	42	31	2.53
VPO/octan-2-one	385	1.3	21.1	25	45	30	2.67
VPO/octan-3-one	385	1.9	21.6	25	47	28	1.92
VPO/butanone	385	0.9	16.4	25	43	32	2.98
VPO/hexan-2-one	385	1.7	28.5	22	53	25	2.45
VPO/octanal	385	1.0	8.5	28	37	35	1.60
"*anhydrous* $VOPO_4$"/octan-1-ol	385	3.6	35.5	22	57	21	1.45
"*anhydrous* $VOPO_4$"/octan-2-ol	385	3.3	34.2	21	58	21	1.42
"*anhydrous* $VOPO_4$"/octan-3-ol	385	1.2	15.5	24	47	29	2.09
"*anhydrous* $VOPO_4$"/hexan-1-ol	385	2.7	29.6	18	55	27	1.32
"*anhydrous* $VOPO_4$"/hexan-2-ol	385	2.5	28.7	23	67	10	1.73
"*anhydrous* $VOPO_4$"/hexan-3-ol	385	1.4	11.5	27	44	29	1.47
VPO^X/octan-1-ol[a]	385	3.1	25.8	29	58	13	1.63
VPD^X/octan-1-ol[a]	385	1.7	13.2	23	50	27	1.21

[a] The superscript X denotes excess H_3PO_4 method.

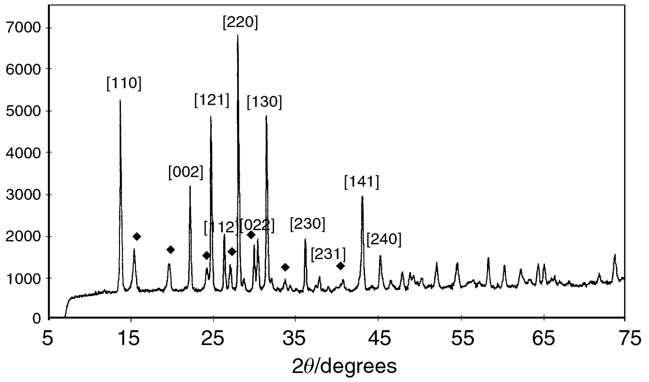


Fig. 8 Powder XRD pattern of the product of reduction of γ-$VOPO_4$ with isobutanol, (◆) denotes lines attributed to $VOHPO_4 \cdot 0.5H_2O$.

Based on a combination of the powder XRD and Raman spectroscopy studies, it can be concluded that the activated catalysts comprise disordered material, together with non-transformed $VO(H_2PO_4)_2$, $VOPO_4$ phases and possibly $VO(PO_3)_2$. It is possibly the presence of the $VOPO_4$ phases that gives rise to the poor maleic anhydride selectivity since it is known that these materials tend to give very poor selectivity for *n*-butane oxidation.[18]

The catalysts derived from $VO(H_2PO_4)_2$ were examined using XPS and the results are summarised in Table 2. The mean surface P/V ratio was determined to be 2.9 for the catalysts. The charge-corrected $V(2p_{3/2})$ binding energy for all samples is 518.0 ± 0.2 eV which is characteristic of V^{5+},[19] whereas the binding energy for V^{4+}, estimated from a plot of experimental binding energy *vs.* oxidation state (inset, Fig. 11) is 516.7 eV. Fig. 11 shows the V(2p)–O(1s) region for one of the catalyst samples with the positions of V^{5+} and V^{4+} indicated. Although the surface comprises vanadium predominantly in the 5+ oxidation state, we cannot completely rule out a contribution from a small surface concentration of V^{4+}.

The O(1s) spectra exhibit an asymmetry to higher binding energy which has previously been assigned to the presence of surface hydroxy groups.[17] Deconvolution of instrumental broadening from the profiles[24] confirmed the presence of a discrete second component, ruling out differential charging as the origin of the apparent asymmetry, and the original data

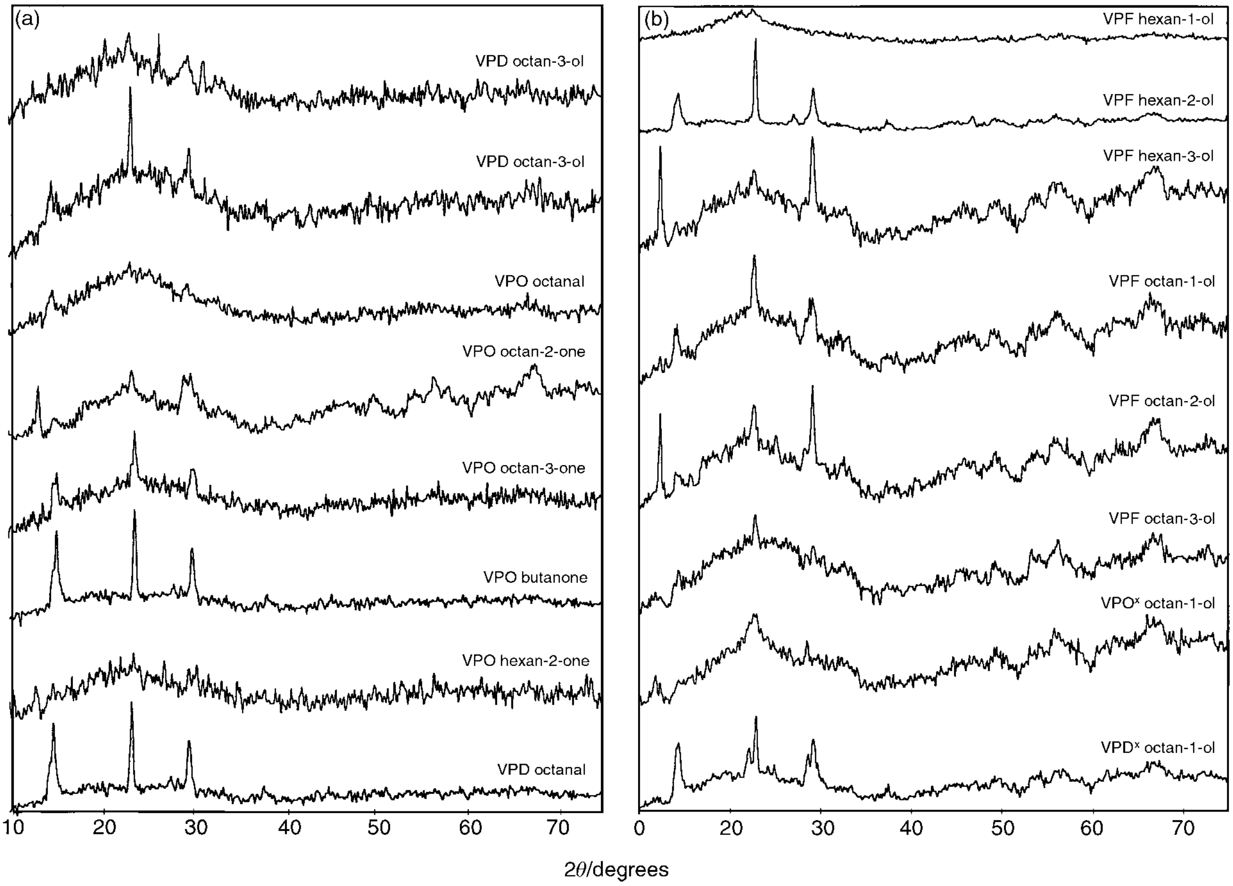


Fig. 9 Powder XRD patterns of catalysts after reaction.

Table 2 Photoelectron binding energies and derived atomic ratios for the catalyst samples derived from $VO(H_2PO_4)_2$. Binding energies are charge-corrected by reference to the C 1s peak assumed to have a binding energy of 285.0 eV

	Binding energies/eV				Ratios	
Catalyst	$V(2p_{3/2})$	O(1s)		P(2p)	OH/O^{2-}	P/V
VPO : octanan-2-one	517.9	532.2	533.9	134.8	0.52	2.75
VPD : octan-3-ol	517.9	532.3	534.1	134.8	0.32	2.55
VPO : octanol	517.9	532.3	534.1	134.9	0.41	3.05
VPO : octan-3-one	517.8	531.7	534.5	135.0	0.26	3.40
VPO : butanone	518.3	532.8	534.7	135.1	0.27	2.80
VPD:	518.2	532.6	534.5	135.3	0.21	2.95

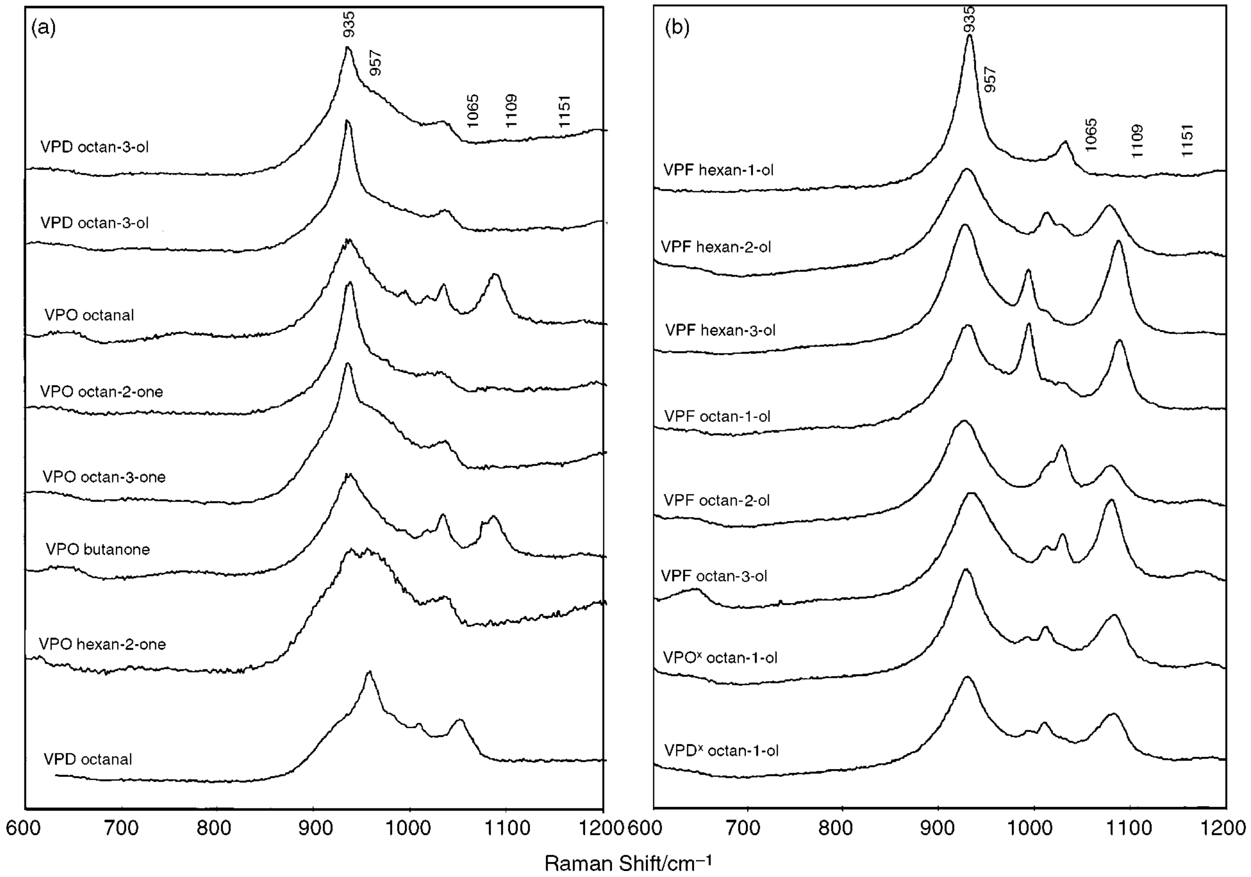


Fig. 10 Raman spectra of catalysts after reaction.

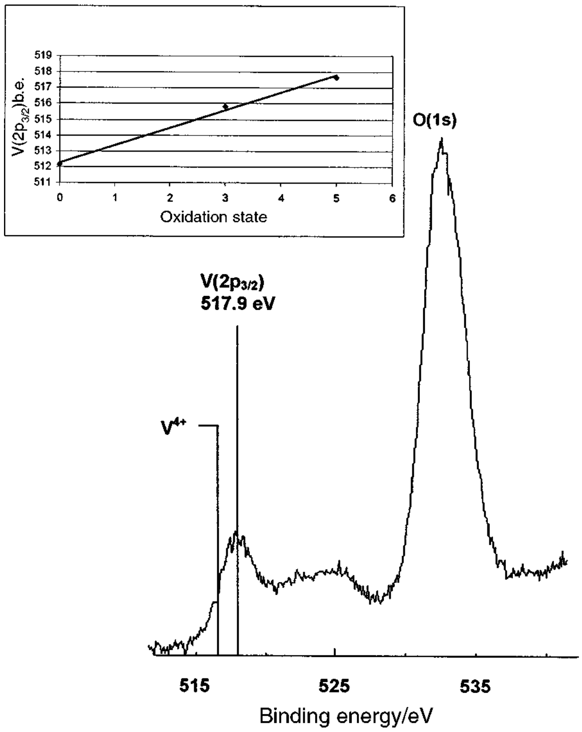


Fig. 11 V(2p) + O(1s) spectral region for the sample corresponding to the curve-fit in Fig. 12. The binding energy scale has been charge-corrected relative to a C(1s) binding energy of 285.0 eV. The expected binding energy position for V^{4+} species is estimated from the plot of V(2p$_{3/2}$) binding energy *vs.* oxidation state shown inset (data from ref. 19), and is indicated on the spectrum.

were, therefore, subjected to a curve-fit analysis (Fig. 12). Unconstrained fits to O(1s) spectra from 4 samples identified two components with binding energies of 532.5 ± 0.2 eV and 534.4 ± 0.3 eV, with a constant splitting of 1.85 eV. The ratio of the intensity of the higher binding energy peak to that of the lower binding energy peak was determined to be in the range 0.21–0.52, values which are much lower than that reported previously (1.45).[17] The surface P/V ratio is lower than that observed in the previous study[17] for initial high maleic anhydride selectivities. Surface enrichment for phosphorus is well documented for vanadium phosphates.[1] For

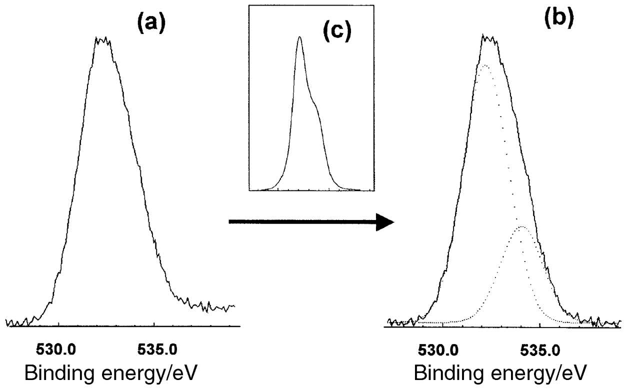
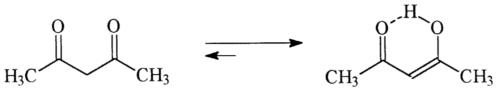


Fig. 12 Illustration of the analysis procedure applied to the O(1s) spectra from the catalysts derived from $VO(H_2PO_4)_2$. The raw spectrum (a) is subjected to a non-linear background removal procedure followed by curve-fitting (curve (b)), making use of the deconvoluted profile (c) both to confirm the existence of 2 spectral components and to estimate component parameters.

$(VO)_2P_2O_7$, the surface P/V ratio is typically *ca.* 2 compared with a bulk ratio of 1. In the case of $(VO)_2P_2O_7$, the excess surface phosphorus has been proposed to act as a diffusion barrier that isolates the active sites. For the catalysts prepared from $VO(H_2PO_4)_2$ the surface P/V ratio is somewhat higher and yet the selectivity is considerably lower. This suggests that excess surface P does not act as a diffusion barrier. In this case, it is more likely that the excess phosphorus changes the surface acidity leading to the preferential adsorption and further reaction of maleic anhydride.

Comments on the formation of $VO(H_2PO_4)_2$ using aldehydes and ketones

Johnson *et al.*[12] showed that, in the preparation of $VOHPO_4 \cdot 0.5H_2O$ from the alcohol reduction of V_2O_5 and H_3PO_4, the alcohol (propan-2-ol and butan-2-ol) oxidised to the corresponding ketone. Cornaglia *et al.*[25] found that, using benzyl alcohol and isobutanol in a similar reaction, benzaldehyde and benzoic acid were formed as oxidation products. Use of aldehydes and ketones as reducing agents, in place of alcohols, would result in different oxidation products, since both can be oxidised to the corresponding carboxylic acid. However, the oxidation of a ketone to a carboxylic acid must involve carbon–carbon bond cleavage and it is unlikely that the reaction conditions used in this study would facilitate such a reaction. In the present study, no reaction was observed for a ketone or aldehyde with $VOPO_4 \cdot 2H_2O$ (*i.e.* the VPD method) unless a small amount of H_3PO_4 was added. Refluxing $VOPO_4 \cdot 2H_2O$ and H_3PO_4 in water yielded no reaction, which is not unexpected since $VOPO_4 \cdot 2H_2O$ is prepared in aqueous solution with a large excess of H_3PO_4 and no reaction is observed. We propose that the involvement of an aldehyde or ketone as a reducing agent is *via* the enol tautomer. For most aldehydes and ketones only a small proportion of the enol tautomer is present, but in the presence of a Brønsted acid the equilibrium is more favourable and more enol is formed. Some carbonyl compounds, *e.g.* β-diketones, exist mainly in the enol form. For example, penta-2,4-dione is stabilised in the enol form by forming a conjugated enone and an intramolecular hydrogen bond between the enol proton and the remaining carbonyl oxygen.



penta-2,4-dione Z-4-hydroxypent-3-en-2-one

As a demonstration that the ketones and aldehydes operate as reducing agents in the enol form, $VOPO_4 \cdot 2H_2O$ was reacted with penta-2,4-diene in the absence of added H_3PO_4 and $VO(H_2PO_4)_2$ was formed as the exclusive product.

The observation that $VO(H_2PO_4)_2$ can be readily formed from V_2O_5 and H_3PO_4 when reacted with aldehydes and ketones is of significance for the preparation of the commercially used hemihydrate precursor, $VOHPO_4 \cdot 0.5H_2O$. The hemihydrate precursor is typically prepared using V_2O_5 and H_3PO_4 with an alcohol as a reducing agent. As noted in an earlier study[12] the alcohol is oxidised to an aldehyde and ketone and, consequently, it is probable that some $VO(H_2PO_4)_2$ will be formed, albeit in trace quantities. Unless this is removed from the precursor, the $VO(H_2PO_4)_2$ will transform on activation in butane/air to give a catalyst that is less selective than the active phases derived from $VOHPO_4 \cdot 0.5H_2O$. This was recognised by Hutchings and Higgins[4,13] who demonstrated that a simple water extraction procedure could be used to remove the water soluble $VO(H_2PO_4)_2$ impurity from $VOHPO_4 \cdot 0.5H_2O$. The significance of the present study is that $VO(H_2PO_4)_2$ is probably present in many vanadium phosphate catalyst preparations and may be responsible for poor catalytic or variable performance.

Acknowledgements

We thank the EPSRC for financial support.

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