Amorphous Vanadium Phosphate Catalysts Prepared using Precipitation with Supercritical CO₂ as an Antisolvent

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Abstract

A new preparative route for vanadium phosphate catalysts is described using supercritical CO₂ as an antisolvent. The amorphous microspheroidal VPO produced is shown to be more active than comparable crystalline VPO catalysts for the selective oxidation of *n*-butane to maleic anhydride and, furthermore, does not require an extensive pre-treatment or activation period to establish full catalytic activity. VPO catalysts prepared using supercritical CO₂ as an antisolvent maintain their amorphous nature throughout the catalyst test period. In contrast, amorphous VPO catalysts can also be prepared using liquid CO₂ as antisolvent, or by solvent evaporation *in vacuo*, however, these materials are found to partially crystallise during the oxidation of *n*-butane. The wholly amorphous catalysts are characterised using transmission electron microscopy, X-ray absorption spectroscopy, ³¹P spin echo mapping NMR spectroscopy and X-ray photoelectron spectroscopy. The role of amorphous material in vanadium phosphate catalysis is discussed in detail.

Keywords: *n*-butane oxidation to maleic anhydride, amorphous and crystalline vanadium phosphates, antisolvent precipitation using supercritical CO₂

Introduction

Vanadium phosphate compounds are utilised commercially as catalysts for the synthesis of maleic anhydride for the partial oxidation of *n*-butane. Consequently, vanadium phosphate catalysts have been extensively studied (1-4). The current commercial catalysts are prepared from *in situ* activation (5) of VOHPO₄·0.5H₂O under reactions conditions (6,7). The resulting catalyst comprises a complex mixture of (VO)₂P₂O₇ in combination with α- and δ-VOPO₄ phases (6). Some researchers favour V⁴⁺ phases, e.g. (VO)₂P₂O₇, as the sole active phase (8-11). However, *in situ* Raman spectroscopy (5) suggests that combinations of V⁴⁺ and V⁵⁺ phases are required for the catalyst to exhibit high activity

and selectivity to maleic anhydride. Indeed, recently Coulston *et al.* (12) have shown that the presence of V⁵⁺ appears to be essential for the initial activation of *n*-butane, an observation that is essentially in agreement with earlier TAP pulse reactor experiments (13). To some extent, the debate concerning the involvement of specific VPO phases is complicated by the observation that many vanadium phosphate catalysts contain significant amounts of disordered material (5,6,9-11,14-29). Some studies suggest the amorphous material is an active component (5,6,15,18,19,26-29), whereas others consider this not to be the case (8-11,22). Amorphous VPO compounds have been used as one way to secure *in situ* regeneration in industrial reactors (30) by using a high

temperature treatment with pure *n*-butane. Indeed, the transformation of the crystalline precursor VOHPO₄·0.5H₂O to the crystalline catalyst (VO)₂P₂O₇ is observed to involve the transformation of significant amounts of amorphous material (6). Until recently, VPO catalysts containing solely amorphous material have not been investigated as active catalysts. In our earlier communication (31), we presented our initial results showing that an amorphous vanadium phosphate could be generated from precipitation using supercritical CO₂ as an antisolvent. In this paper, we extend these initial results and discuss the potential role of amorphous vanadium phosphate catalysts for the partial oxidation of *n*-butane.

Experimental

Catalyst preparation

Preparation of crystalline VOHPO₄·0.5H₂O

The hemihydrate VOHPO₄·0.5H₂O was prepared using three distinct routes, denoted VPA, VPO and VPD:

The *VPA hemihydrate* was prepared by dissolving V₂O₅ (6.06 g, Strem) in aqueous HCl (35%, 79 ml) at reflux for 2 h. H₃PO₄ (8.91 g, 85%, Aldrich) was added and the solution refluxed for a further 2 h. The solution was subsequently evaporated to dryness and the resulting solid was refluxed in water (20 ml H₂O/g solid) for 1 h. It was then filtered hot, washed with warm water, and then dried in air (110°C, 16 h).

The *VPO hemihydrate* was prepared by refluxing V₂O₅ (11.8 g, Strem) with H₃PO₄ (16.49 g, 85%, Aldrich) in *isobutanol* (250 ml) for 16 h. The light blue solid was recovered by filtration, washed with *isobutanol* (200 ml) and ethanol (150 ml, 100%). The solid was refluxed in water (9 ml H₂O/g solid) for 1 h, filtered hot, and dried in air (110°C, 16 h).

The *VPD hemihydrate* was prepared from the dihydrate compound VOPO₄·2H₂O. V₂O₅ (5.0 g, Strem) and H₃PO₄ (30 ml, 85%, Aldrich) were refluxed 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). Powder X-ray diffraction and laser Raman spectroscopy confirmed this solid was VOPO₄·2H₂O. This VOPO₄·2H₂O phase (4 g) was refluxed with *isobutanol* (80 ml) for 21 h and the resulting hemihydrate was recovered by filtration and dried in air (110°C, 16 h).

Catalyst preparation using supercritical CO₂ as an antisolvent

A solution of H₃PO₄ (1.8 g, 100%, Aldrich) in *isopropanol* (120 ml) was refluxed with VOCl₃ (1.6 ml, Aldrich) for 16 h to give a blue solution. The resulting *isopropanol* solution was processed using supercritical CO₂ to precipitate a vanadium phosphate using the apparatus shown schematically in Figure 1 with the following methodology. The *isopropanol* solution was pumped through a fine capillary (220 µm i.d.) into a precipitation vessel containing concurrently flowing CO₂. The CO₂ can act as an effective antisolvent when it is either a liquid (>42 bar at 20°C) or a supercritical fluid

(T_c=31.3°C, P_c=72 bar). CO₂ was pumped as a liquid using a modified HPLC pump at pressures up to 110 bar; the system

Figure 1: Schematic of the apparatus for the precipitation of vanadium phosphates using supercritical or liquid CO₂. BPR, back pressure regulator, PV, precipitation vessel, P, pumps.

pressure is maintained by a back pressure regulator (BPR) and flow rates of the CO₂ and *isopropanol* solution can be set independently. To achieve supercritical conditions, the precipitation vessel (PV) is held in a gc oven allowing control of the temperature from ambient to *ca.* 100°C. The CO₂ passes through a length of coiled tubing in the oven and is heated through its critical point, becoming supercritical. As the vanadium phosphate solution exits the capillary, the alcohol and CO₂ diffuse into each other causing the *isopropanol* to expand, hence reducing its solvent power. The higher temperature together with the removal of the organic solvent enable rapid precipitation of the vanadium phosphate. The catalyst precursor denoted VPO_{SCP} is collected on a filter bed. The *isopropanol* solution was pumped at 0.1 ml/min through the capillary along with excess CO₂ which was pumped at 7 ml/min. The system pressure was held constant at 110 bar and the precipitation vessel maintained at 60°C. Experiments were typically conducted for 3 h which resulted in the synthesis of 0.2 g of solid. Similar experiments were conducted using *isobutanol* as the alcohol solvent since this is the alcohol typically used in the conventional synthesis of VOHPO₄·0.5H₂O (32). A catalyst was also prepared using the same methodology but using liquid CO₂ (P_{CO₂} = 60 bar) at 15°C.

Two further catalysts were prepared using similar methodologies. First a Co-containing catalyst was prepared using supercritical CO₂ precipitation for a modified solution containing 1 mol% Co. Cobalt has been previously identified as a promising promoter element for vanadium phosphate catalysts (4). More specifically, cobalt acetylacetonate (0.0288 g, Aldrich) was dissolved in the *isopropanol* vanadium phosphate solution previously described (100 ml) and the resulting solution was refluxed for 5 h. This solution was then processed using supercritical CO₂ as described previously. Secondly, a solution was prepared by adding acetylacetone (0.084 g, Aldrich) to the *isopropanol* vanadium phosphate solution (250 ml) and the resulting solution was refluxed for 5 h, prior to being processed using supercritical

CO₂ as described above. Attempts to obtain a solid from the standard *isopropanol* vanadium phosphate solution by solvent removal using distillation were unsuccessful. However, slow evaporation at 60°C under vacuum using a Schlenk line did lead to the formation of a solid which was also investigated as a potential catalyst.

Catalyst testing

The oxidation of *n*-butane was carried out using a microreactor with a standard mass of catalyst (0.5 g). *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 then 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 $\pm 1^\circ\text{C}$. Carbon mass balances of $\geq 97\%$ were typically observed. Catalyst precursors were heated *in situ* (1.5% *n*-butane in air) at 400°C by heating the sample from room temperature at a rate of 3°C/min.

Catalyst characterisation

A number of techniques were used to characterise the catalyst structure. Powder X-ray diffraction (XRD) was performed using an Enraf Nonius FRS90 X-ray generator with a Cu-K α 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 ($\lambda = 514.532\text{ nm}$).

Scanning electron microscopy (SEM) was performed on a Hitachi S26YO-N instrument operating at 20kV and fitted with a Link Systems EDX spectrometer. Transmission electron microscopy (TEM) observations were made with a JEOL 2000 EX high-resolution electron microscope operating at 200 kV. The instrument had been fitted with a low-light level TV camera and frame-averaging system to allow us to use very low illumination conditions. This latter condition is essential for studying these beam-sensitive vanadium phosphorus oxide compounds. Samples suitable for TEM analysis were prepared by dispersing the catalyst powder onto a lacy carbon film supported on a copper mesh grid.

The ³¹P NMR measurements were performed on a Bruker MSL 300 NMR spectrometer. The ³¹P spin-echo mapping method has been shown by Li *et al.* (33) and Sananes *et al.* (34) to be a very powerful technique for evaluating the relative proportion of V⁵⁺ and V⁴⁺ ions surrounding the P atoms in vanadium phosphate compounds independently of the crystallinity. The ³¹P NMR spin-echo spectra were recorded under static conditions, using a 90°x-τ-180°y-τ acquisition sequence. The 90° probe duration was 4.2 μs and τ was 20 μs. For each sample, the irradiation frequency was varied in increments of 100 kHz above and below the ³¹P resonance of H₃PO₄. The number of spectra recorded was dictated by the frequency limits beyond which no spec-

tral intensity was detectable. The ³¹P NMR spin-echo mapping information was then obtained by super-position of all the spectra.

X-ray photoelectron spectroscopy (XPS) was used to determine the P/V surface atomic ratio of the catalysts. XPS measurements were made using a VG ESCA 3 photoelectron spectrometer employing an Al-K α 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 (35).

X-ray absorption spectroscopy (XAS) in the soft energy range between 100 eV and 1000 eV represents a surface sensitive method if applied in the electron yield mode. Complimentary to photoelectron spectroscopy XAS probes the unoccupied states. The spectra can be correlated more or less directly to the unoccupied density of states (DOS). Since the process is local and governed by dipole selection rules the data are related to the site- and symmetry-selected DOS. No long range order is necessary and the method is therefore extremely useful to characterise amorphous material. For a long period XAS has been solely used under UHV conditions, however, we have developed a new set-up which allows the collection of X-ray absorption data in the total electron yield mode under relatively high pressure conditions (pressure = 2 mbar). This renders it possible to study the surface of a catalyst *in situ*, i.e. under conditions that are similar to the normal working conditions.

The XAS experiments were performed with a special reactor cell consisting of two stainless-steel chambers. Details about the set-up and the data processing can be found in the literature (36, 37). Experiments were carried out at the undulator beamline UE/56-2 at the third generation Berliner Synchrotron Radiation Facility BESSY (38). The near edge X-ray absorption fine structure (NEXAFS) was analysed, i. e. the strong variations of the absorption coefficient just at the absorption edge. For the *in situ* experiments a continuous flow of 1.5 vol% *n*-butane in He and oxygen were dosed via two calibrated mass flow controllers at a total mass flow of 17.5 ml/min. The partial pressures of the *n*-C₄H₁₀/He mixture and the oxygen were 1.6 mbar and 0.4 mbar, respectively, resulting in a total pressure in the reactor of 2 mbar during the NEXAFS measurements. The sample was heated in the reaction mixture up to 400°C by a resistive heater. The catalyst powder (50 mg) was pressed into a flat pellet (diameter 13 mm) in order to mount it on the stainless steel sample holder. Part of the gas phase in the reactor was sampled via a capillary (diameter 3 mm) just above the sample and analysed with a quadrupole mass spectrometer. The photon energy of the NEXAFS spectra was calibrated by the π^* -resonance of molecular oxygen at 530.8 eV. The resolving power $E/\Delta E$ was about 3000. Vanadium L₃-edge spectra were analysed by a least squares fit applying Gauss-Lorentz profiles considering experimental and intrinsic broadening.

Results

Catalyst evaluation

A series of vanadium phosphate catalyst precursors were prepared from the *isopropanol* vanadium phosphate solution using the following methods: (a) precipitation with supercritical CO₂, (b) precipitation with liquid CO₂, and (c) evaporation of the solution on a Schlenk line under vacuum. The precursors were denoted VPO_{SCP1}, VPO_{LP}, VPO_{EP} respectively. These precursors were evaluated as catalysts for the partial oxidation of *n*-butane to maleic anhydride and the results are shown in Tables 1 and 2. For comparison, the results for typical catalysts prepared by the standard VPA, VPO and VPD procedures are also shown.

Table 1: Catalytic activity of vanadium phosphate catalysts.

Preparation Route	Intrinsic Activity ^b			
	Maleic anhydride selectivity (%) ^a		Surface area (m ² g ⁻¹)	Intrinsic Activity (mol MA m ⁻² h ⁻¹)
	S ₁₀ ^{MA}	S ₂₀ ^{MA}		
VPA	68	52	4	2.8 x 10 ⁻³
VPO	85	72	14	2.7 x 10 ⁻⁵
VPD	70	68	43	2.4 x 10 ⁻⁵
VPO _{SCP1}	-	45	4	4.6 x 10 ⁻⁵
VPO _{SCP2} ^c	-	42	3	0.42 x 10 ⁻⁵
VPO _{LP}	-	39	6	2.9 x 10 ⁻⁵
VPO _{EP}	42	-	8	1.7 x 10 ⁻⁵
VPO _{CoSC}	28 ^c	28	5	1.0 x 10 ⁻⁵
VPO _{acacSC}	37	37	9	2.0 x 10 ⁻⁵

^a S₁₀^{MA} and S₂₀^{MA} = maleic anhydride selectivity at 10% and 20% conversion respectively.

^b GHSV = 2400 h⁻¹ for VPA, VPO, VPD, VPO_{SCP1}, VPO_{LP} and VPO_{EP} catalysts; 3000h⁻¹ for VPO_{SCP2}; and 4070 h⁻¹ for VPO_{CoSC} and VPO_{acacSC} catalysts. The reaction temperature was 400°C and the concentration of butane in air was 1.5% by volume for all catalysts.

^c selectivity at 4% conversion

It is apparent that none of the three catalysts requires an activation period to establish the steady state catalyst performance which is generally associated with vanadium phosphate catalysts (1,5,6). During this activation period, it is usual that catalysts derived from crystalline hemihydrate VOHPO₄·0.5H₂O undergo a structural transformation to (VO)₂P₂O₇ and VOPO₄ phases (5,6). However, it is clear that, for the precursors VPO_{SCP1}, VPO_{LP} and VPO_{EP}, this activation period is absent (Figures 2). The catalysts derived from VPO_{SCP1}, VPO_{LP} and VPO_{EP} all have low surface areas of 4, 6, and 8 m² g⁻¹ respectively, when compared with the standard VPO (14 m² g⁻¹) and VPD (43 m² g⁻¹) materials. The intrinsic activity for these catalysts are shown in Table 1 and Figure 2. From these data, it is clear that the catalyst derived from VPO_{SCP1} has a significantly higher intrinsic activity for the production of maleic anhydride. This preparation method has been repeated many times and the enhanced activity is always observed. Interestingly, the catalyst derived from the precursor prepared in liquid CO₂ which has an intrinsic activity higher than the

Table 2 Catalytic performance of vanadium phosphate catalysts^a

Preparation Route	Selectivity (%)			
	Butane Conversion (%)	maleic anhydride	CO	CO ₂
VPA ^b	11	51	41	7
VPO ^b	27	52	34	14
VPD ^b	62	64	21	14
VPO _{SCP1} ^b	16	44	30	26
VPO _{SCP2} ^c	30	24	0	76
VPO _{LP} ^b	17	39	23	38
VPO _{EP} ^b	11	40	31	29
VPO _{CoSC} ^d	3.5	31	48	21
VPO _{acacSC} ^d	9.6	39	28	33

^a reaction conditions : 400°C, 1.5% *n*-butane in air

^b GHSV = 2400 h⁻¹

^c GHSV = 3000h⁻¹

^d GHSV = 4070 h⁻¹

Figure 2 The intrinsic activity for maleic anhydride (mol h⁻¹ m²) with time on stream. For VPA/VPO/VPD catalysts GHSV = 1200 h⁻¹, for all other catalysts GHSV = 2400 h⁻¹.

VPA/VPO/VPD catalysts, whereas the catalyst derived from the sample prepared by evaporation, VPO_{EP}, exhibited a similar intrinsic activity to the VPA/VPO/VPD catalysts.

In a further set of experiments, a catalyst was prepared from an *isobutanol* solution of VOCl₃ and H₃PO₄ treated with supercritical CO₂. The material, denoted VPO_{SCP2}, was evaluated as a catalyst and it is apparent that this material is less effective as a catalyst as compared with VPO_{SCP1} (Tables 1 and 2).

Two further catalysts were evaluated, these being prepared from the Co-doped *isopropanol* solution (VPO_{CoSC}) and the acetylacetonate-doped *isopropanol* solution (VPO_{acacSC}). Interestingly, the VPO_{CoSC} catalyst is quite inactive for the oxidation of *n*-butane. The VPO_{acacSC} sample is active, but is significantly less so than the catalyst derived from VPO_{SCP1}. The results with the Co-doped sample are particularly interesting since Co is known to act as a catalyst promoter for the VPA/VPO/VPD derived catalysts. This, therefore, represents a further significant difference between catalysts derived from crystalline VOHPO₄·0.5H₂O and catalysts prepared using supercritical CO₂ as an antisolvent. Analysis of the catalysts prepared using supercritical CO₂ showed that they contained impurities (Fe 8000 ppm, Cr 2000 ppm, Ni 800 ppm) which are considered to originate

from the apparatus used in these initial studies. Hence, the vanadium phosphates prepared in this way may, indeed, involve multiple promoters and these may be present at non-optimal levels. This may be a reason for the poor performance of the catalyst containing additional Co, since high concentration of promoters are known to be less active as catalysts for *n*-butane oxidation to maleic anhydride (4).

The selectivity to maleic anhydride is also compared at 10% and 20% *n*-butane conversion for the catalysts and these data are given in Table 1. The selectivity to maleic anhydride for the material prepared using supercritical CO₂ as an antisolvent are lower than the crystalline vanadium phosphates when compared at the same conversion level. This, coupled with the higher level of activity, may indicate that, at present, we have not achieved an optimal distribution of the active sites on the catalyst surface.

Catalyst characterisation

The precursors and the catalysts derived from VPO_{SCP1}, VPO_{SCP2}, VPO_{LC}, VPO_{EP}, VPO_{CoSC} and VPO_{acacSC} were examined using powder XRD and laser Raman spectroscopy. All the precursors were found to be amorphous by X-ray diffraction and, furthermore, no Raman spectra could be obtained from these samples. Following the catalyst evaluation in the microreactor, the samples VPO_{SCP1}, VPO_{SCP2}, VPO_{CoSC} and VPO_{acacSC} remained amorphous to X-ray diffraction and, again, no Raman spectra could be obtained. However, the samples derived from precipitation with liquid CO₂ (VPO_{LP}) and from evaporation (VPO_{EP}) were found to have crystallised during the catalyst evaluation in the microreactor. The powder XRD and laser Raman spectra for VPO_{LP} and VPO_{EP} are shown in Figure 3 and it is apparent that the crystalline material is a mixture of (VO)₂P₂O₇ and VOPO₄ phases, as has been observed in the conventional VPA/VPO/VPD catalysts. It is therefore entirely consistent that the intrinsic activities for the production of maleic anhydride are similar for these catalysts (Figure 2).

³¹P NMR spectroscopy confirms the presence of crystalline material (Figure 4). The spin echo mapping spectrum of the VPO_{EP} precursor has a signal centred at 1000 ppm which is characteristic of V⁴⁺-V⁵⁺ dimers. The VPO_{EP} precursor has several contributions to the signal: 1000 ppm which is characteristic of V⁴⁺-V⁵⁺ dimers, 650-600 ppm and 250 ppm which is due to V⁴⁺-V⁵⁺ dimers associated with V⁵⁺ sites and 0 ppm due to V⁵⁺ sites. Both the samples have a single sharp resonance at 0 ppm after catalyst testing which is characteristic of V⁵⁺ and ³¹P MAS NMR was used to resolve the nature of the V⁵⁺ material present (Figure 4(b)). For the VPO_{EP} catalyst the spectrum is characteristic of δ-VOPO₄, with signals at -10 ppm and -21 ppm. The VPO_{LP} material also has the characteristic δ-VOPO₄ spectrum but has additional resonances at 27 ppm and 36 ppm, which are a result of V⁵⁺ microdomains in the catalyst.

The catalysts derived from precipitation using supercritical CO₂ were then examined in further detail. First, the precursors and activated catalysts were examined using TEM and representative micrographs of these materials are

shown in Figure 5. The VPO_{SCP1} precursor material (Figure 5(a)), consists of discrete spherical particles ranging between 75 nm and 5 μm in size, although most lie between 75 nm and 1 μm in diameter. These particles show no diffraction contrast (only thickness contrast) and are very prone to electron beam damage. The activated VPO_{SCP1} catalyst prepared from the *isopropanol* solution (Figure 5(b)) comprises agglomerated spherical particles which show the initial signs of sintering. Several spherical voids, *ca.* 0.2 nm in diameter, are usually seen within each particle, arising presumably from the loss of water during activation. Low-dose, high resolution electron microscopy (HREM) imaging experiments on both the VPO_{SCP1} precursor and activated catalysts showed no sign of lattice fringes or nanocrystalline order; only amorphous speckle contrast is seen. Selected area electron diffraction analysis of the precursor and activated catalysts derived from VPO_{SCP1} show them to be amorphous. This is consistent with the fact that the particles show no crystallographic faceting and adopt a minimum surface area (i.e. spherical) morphology. In the VPA/VPO/VPD derived catalysts, the activation procedure in *n*-butane/air always generates a considerable fraction of crystalline (VO)₂P₂O₇, together with some VOPO₄ polymorphs (32). These crystalline phases are readily identifiable by powder X-ray diffraction, HREM and electron diffraction. We consider that the material VPO_{SCP1}, either as the precursor or the activated catalyst, comprises a stable mixed P₂O₅-V₂O₅ glassy phase. This is entirely feasible since both P₂O₅ and V₂O₅ satisfy Zachariasen's rules for glass formation (40) and are completely miscible. In fact, even heating VPO_{SCP1} in pure N₂ at 750°C for 6 h resulted in the formation of a relatively minor amount (i.e. less than 5 vol%) of nanocrystalline (VO)₂P₂O₇. A similar treatment of VOHPO₄·0.5H₂O derived from the VPA/VPO/VPD methods would result in complete crystallisation to (VO)₂P₂O₇. The precursor VPO_{SCP2}, prepared using *isobutanol* as solvent, showed identical morphology to VPO_{SCP1} (Figure 5(c)). However, in contrast to VPO_{SCP1}, the VPO_{SCP2} material after activation (Figure 5(d)) showed the presence of a significant proportion of nanocrystalline (VO)₂P₂O₇ that had formed during the catalyst evaluation period. Interestingly, this catalyst was less active for the formation of maleic anhydride. This demonstrates that the alcohol used as solvent can affect the nature of the material prepared using supercritical CO₂ as an antisolvent.

³¹P spin echo mapping NMR spectroscopy also confirms that both the precursor and catalyst prepared from VPO_{SCP1} are distinctly different from the conventional VOHPO₄·0.5H₂O derived precursors and activated catalysts (Figure 6). In Figure 6(a), the presence of a high number of V⁴⁺/V⁵⁺ dimers at 1100 ppm are clearly visible. A small contribution from V⁵⁺ sites at 0 ppm is also observed and this becomes more pronounced in intensity following the catalyst testing (Figure 6(b)) which demonstrates that some modification of the material has occurred during the catalyst testing. Significantly, in both the precursor and catalyst derived from VPO_{SCP1}, there is no significant contribution at 2400 ppm indicating the absence of any crystalline (VO)₂P₂O₇ phase.

Figure 3 Characterisation of catalysts derived from VPO_{LP} and VPO_{EP}: (a) XRD and (b) laser Raman spectra. Key: ■ α -VOPO₄, ● β -VOPO₄, □ γ -VOPO₄, ◆ δ -VOPO₄, X (VO)₂P₂O₇.

XPS of the new amorphous VPO_{SCP1} before and after catalyst testing, also confirms it to be different from the VPA/VPO/VPD precursors and catalysts. Conventional catalysts based on (VO)₂P₂O₇ are known to be significantly enriched with phosphorus at the surface (1,32). For the amorphous VPO_{SCP1} derived precursor and activated catalyst, the P/V ratio is closer to unity. Semi-quantitative SEM-EDX analysis of the bulk composition was also performed on the VPO_{SCP1} materials. Both the precursor and the activated catalysts are rich in P with bulk P/V ratios in the range

1.2 < P/V < 1.5. Treatment of VPO_{SCP1} in pure N₂ at 750°C for 6 h caused the P/V ratio to fall to 0.5 < P/V < 0.7. This latter observation is consistent with the previous reports that P and O are preferentially lost from P₂O₅-V₂O₅ glasses when heated (40).

In Figure 7 the vanadium L_{2,3}- and the oxygen K-absorption edge of the totally amorphous catalyst prepared after the new supercritical method (VPO_{SCP1}), a crystalline catalyst prepared using the alcoholic route (VPO) and a supercritical catalyst doped with cobalt (VPO_{CoSC}) are displayed. As indi

Figure 4 ³¹P NMR spectroscopy of the materials derived from VPO_{LP} and VPO_{EP}: (a) spin echo mapping spectra of the precursors and catalysts, (b) MAS spectra of the catalysts.

cated, the O K-edge follows directly in photon energy after the vanadium L-edges. The vanadium L-edges can be separated in structures belonging to the V2p_{3/2} → V3d (V L₃-edge) and to the V2p_{1/2} → V3d (V L₂-edge) transition respectively. At the oxygen edge (approximately at photon energies higher than 528 eV) there are contributions from hybridisation of O2p states with vanadium and O2p/phosphorus states superimposed. By comparison with reference phosphates it can be concluded that the first absorption resonances from 529–535 eV are mainly contributed

by O2p/V3d states while the strong features above 534 eV are mainly arising from hybridisation of oxygen and phosphorus molecular orbitals. In the figure it can be seen that all catalysts exhibit three distinct absorption features at 529.3, 530.8 and 532.4 eV, but their intensity ratios vary. While for the catalysts VPO and VPO_{CoSC} the first resonance is the most intensive, all three resonances are almost equal in intensity for the undoped catalyst VPO_{SCP1}. As mentioned above this can be interpreted as a significant difference in the V-O bonding situation for the amorphous sample, which seems to be quite unusual for vanadyl pyrophosphate catalysts. The broad resonance around 538 eV, attributed to O/P hybridised electronic states, is most pronounced at the supercritical catalyst VPO_{SCP1} compared to the normalised intensity at the vanadium edge.

Further analysis was subsequently focused on the V L₃-NEXAFS shown for the above mentioned catalysts VPO_{SCP1}, VPO and VPO_{CoSC} in Figure 8. The vanadyl pyrophosphate catalysts show a very detailed absorption structure at the V L₃-edge. Details of the NEXAFS can be interpreted in a framework which relates peak positions to bond lengths (39). Therefore, analysing the different resonances yields direct information about specific vanadium-oxygen bonds present in the catalyst.

At first sight the three samples show a very similar overall spectral function. The resonance positions obtained by a unconstrained least squares fit do not differ more than 0.2 eV (compare also Table 3, number of assumed resonances for VPO_{SCP1} and VPO_{CoSC} are obtained from the fit for VPO). The intensity proportions are quite similar except for the Co doped catalyst, where the resonance V5 around 517.1 eV is not as dominant as in the other samples. This can be seen clearly in the distribution of the spectral weight reported in Table 4. Comparing the totally amorphous catalyst VPO_{SCP1} and the crystalline VPO, two observations are striking. First, the resonance V7 at 519 eV, present both in VPO and VPO_{CoSC} is almost absent in VPO_{SCP1}. Second the overall shape of the V L₃-absorption edge looks less structured for VPO_{SCP1}. This is expressed by the in average significantly higher width of the fitting profiles. The broadening of absorption resonances is a well known phenomenon for amorphous samples compared to crystalline materials, and is also observed for example with amorphous graphite and HOPG (41). Nevertheless, the NEXAFS are similar giving a hint that the undoped catalysts exhibit a very similar local electronic structure in the information depth of approximately 60 Å. In Table 3, energy positions and V-O-distances according to empirical found relationship between the resonance position at the V L₃-edge and the bond length are given (39). Remarkably, for some strong resonances with extracted bond lengths of 1.7 Å and 1.8 Å (V5 and V6, respectively) no equivalent in the geometric vanadyl pyrophosphate structure obtained by XRD measurements (42) can be found. For comparison these are also reported in Table 3.

In addition to these *ex situ* XAS investigations under vacuum we also performed *in situ* experiments under n-butane oxidation conditions with the totally amorphous material VPO_{SCP1}. The set of spectra at the V L₃-edge under

Table 3 The resonance postions at the V L₃-edge and the extracted bond lengths for different catalysts under *ex situ* conditions

Resonance indices	V1	V2	V3	V4	V5	V6	V7
VPO _{SC} Resonance postion (eV)	514.42	515.06	515.67	516.45	517.21	517.98	519.05
VPO _{SC} V-O bond length (Å)	2.25-2.26	2.14-2.16	2.04-2.07	1.90-1.96	1.77-1.85	1.63-1.74	1.45-1.59
VPO Resonance postion (eV)	514.36	515.94	515.56	516.39	517.16	517.97	519.05
VPO V-O bond length (Å)	2.25-2.26	2.17	2.05-2.08	1.91-1.96	1.78-1.86	1.64-1.75	1.52-1.65
VPO _{CoSC} Resonance postion (eV)	514.22	515.90	515.60	516.29	517.01	517.90	518.78
VPO_{CoSC} V-O bond length (Å)	2.27-2.29	2.17-2.18	2.05-2.08	1.93-1.98	1.80-1.88	1.65-1.75	1.49-1.63

Note: different bond lengths according to assumed models in reference (39). For comparison, Bond length by XRD (42): 2.19 Å - 2.20 Å, 2.07 Å - 2.08 Å, 1.93 Å - 1.95 Å, 1.50 Å - 1.52 Å

Figure 5 Transmission electron micrographs of (a) VPO_{SCP1} prior to catalyst testing, (b) VPO_{SCP1} after catalyst testing, (c) VPO_{SCP2} prior to catalyst testing, (d) VPO_{SCP2} after catalyst testing.

Figure 6 ^{31}P spin echo mapping NMR spectroscopy of (a) the VPO_{SCP1} precursor, (b) the VPO_{SCP1} following catalyst testing, (c) a conventional crystalline $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor, (d) the activated catalyst derived from (c).

Figure 7 X-ray absorption spectra at the $\text{V L}_{2,3}$ - and O K -edges of VPO_{SCP1} , VPO and VPO_{CoSC} . Indicated in the figure is a schematic separation in V L - and O K -absorption edge and areas of main contributions by O-V and O-P electronic orbitals. All spectra were normalised on intensity maximum at the V L_2 -edge.

Figure 8 NEXAFS at the V L_3 -edge of VPO_{SCP1} , VPO and VPO_{CoSC} . The fit profiles used are shown and labelled according to their energetic ordering.

these conditions can be found in Figure 9. It is easy to observe that the NEXAFS changes dramatically ((a) $\rightarrow$ (b)).

Figure 9 *In situ* NEXAFS of VPO_{SCP1} under different reaction conditions: (a) at room temperature in a mixture of *n*-butane/helium/oxygen (1.2/78.8/20) at a total pressure of 2 mbar; (b) in the same reaction mixture at 400°C, (c) in pure oxygen (0.4 mbar) at 400°C. Also shown are the fit profiles used.

Table 4 Spectral weights of resonances V1-V8 for VPO_{SCP1}, VPO and VPO_{CoSC} according to the fit displayed in Figure 8.

VPO _{SCP1}		VPO		VPO _{CoSC}	
V1	1%	V1	0%	V1	0%
V2	5%	V2	5%	V2	5%
V3	7%	V3	10%	V3	8%
V4	11%	V4	7%	V4	9%
V5	43%	V5	45%	V5	24%
V6	22%	V6	15%	V6	33%
V7	5%	V7	12%	V7	13%
V8	6%	V8	6%	V8	8%

The overall spectral weight is shifted to lower photon energies. This shift is caused by a 15% decrease of the intensity of resonance V5. The spectral weight of V4 is strongly increased by a factor of 2.5. This change is partially reversible by switching to pure oxygen (P=0.4 mbar, T=400°C), which causes a decrease of V4 and an increase of V5 (b) → (c). This shows that the surface of the catalyst is highly flexible and its response on the applied conditions becomes visible with *in situ* XAS.

Figure 10 Correlation between the first momentum, E_{centre} , of the spectral distribution at the V L₃-edge and the average oxidation state of the material. E_{centre} is shown for reference compounds with a known oxidation state (●) and the linear relation (solid line) obtained by regression. E_{centre} of VPO_{SCP1} at different reaction conditions ((a)-(c)) as described in Figure 9 are indicated by the dashed lines.

It is well known from low resolution X-ray absorption spectra of vanadium compounds that the position of the maximum of the V L₃-edge can be directly correlated to the oxidation state (43-45). In order to transfer this relationship to the high resolution spectra reported in Figure 8 the momentum ($E_{centre} = \int E \cdot TEY(E) dE$) of the area normalised

spectral distribution at the V L₃-edge was calculated. By calculating E_{centre} for reference compounds with a known oxidation state (V⁵⁺: VOPO₄·2H₂O, β-VOPO₄; V⁴⁺: VOHPO₄·0.5H₂O), and catalysts with independently determined oxidation state (by titration and from the position of the pre-peak at the V K-edge (46)) a linear correlation between E_{centre} and the average oxidation state of the material was found (Figure 10). The oxidation state of the VPO_{SCP1} under different reaction conditions can then be determined by this method. It found that starting from an average oxidation state (V_{ox}) of 4.03 at room temperature (A) the catalyst is then reduced ($V_{ox} = 3.79$) under the butane oxidation conditions applied (B). Heating in pure oxygen (C) results in minor re-oxidation ($V_{ox} = 3.85$). The easy reduction of the catalyst, observed under these conditions, may be one reason for the comparatively low selectivity to maleic anhydride of these materials.

The mass spectra of the gas phase were monitored simultaneously (Figure 11) and this indicates an *n*-butane conversion of 3.5%, detectable by the decrease of the intensity of mass fragments $m/e=43$ and $m/e=41$, after reaching the reaction temperature of 400°C. Under similar reaction conditions a conversion of around 5% is observed for a crystalline VPO catalyst although it must be noted that the crystalline VPO catalyst has a significantly higher surface area and consequently this *in situ* experiment confirms the increased intrinsic activity of the VPO_{SCP1} material. Even if the overall conversion obtained under these low pressure conditions is much less than observed under atmospheric pressure, the relation between the conversion obtained with

Figure 11 Monitored mass spectra of *n*-butane, H₂O and CO₂ during heating of VPO_{SCP1}. Reaction conditions: *n*-butane/He/O₂ = 12/78.8/20, at a total pressure of 2 mbar, temperature ramped from room temperature to 400°C, held for 55 min, then cooled back to room temperature. The arrows indicate the point at which the NEXAFS spectra shown in Figure 9 were obtained.

VPO_{SC} and VPO is quite similar to the ones indicated in Table 1. Initially, on heating, a release of water is detected. This may cause some of the dramatic change in the V L₃-

NEXAFS. Simultaneously CO₂ can be observed. The yield of CO₂ decreases when the sample is maintained under reaction conditions for 55 min, while the *n*-butane conversion remains constant. This might be an indication of the partial oxidation reaction to maleic anhydride, which could not be detected directly by mass spectroscopy in our experiments, perhaps due to condensation problems in unheated parts of the capillary line.

Discussion

Rapid precipitation of a vanadium phosphate from an alcohol solution using supercritical CO₂ as an antisolvent provides a preparation route for an amorphous vanadium phosphate. It is clear that both the alcohol and method of solvent removal are important if the amorphous material is to retain its amorphous character under reaction conditions. When *isopropanol* is used as the solvent and supercritical CO₂ is used as the antisolvent, the resulting amorphous VPO material remains amorphous under reaction conditions. Indeed, subjecting the material to aggressive conditions known to crystallise vanadium phosphate to form well crystalline (VO)₂P₂O₇ (750°C, in flowing He, > 8 h) only leads to a very small amount of crystallisation. However, if the solvent is changed to *isobutanol*, the amorphous material forms some micro crystalline domains of (VO)₂P₂O₇ during the catalyst testing and the material is less active for the selective formation of maleic anhydride. Use of liquid CO₂, in place of supercritical CO₂, also produces an amorphous VPO precursor, but this partially crystallises to (VO)₂P₂O₇ and VOPO₄ during the catalyst test period. Removal of the solvent by evaporation is another route that produces an amorphous precursor but, again, this crystallises during the catalyst test period. It is possible that using supercritical CO₂ affords the most rapid precipitation and that the nature of the alcohol solvent can also influence the precipitation process. It is interesting to note that addition of acetylacetone to the *isopropanol* solvent and the use of supercritical CO₂ as an antisolvent produces an amorphous VPO material that remains amorphous after being used as a catalyst. However, in this case the amorphous VPO material is less active on the basis of intrinsic activity. We have previously shown, for catalysts derived from crystalline VOHPO₄·0.5H₂O, that the addition of low levels of ketones can significantly influence the catalytic performance (47) and it is possible that this effect is also maintained for this catalyst preparation method.

At the present stage of this work, the major problems that require attention concern the surface area of the amorphous material, the selectivity to maleic anhydride and the levels of adventitious promoters that are present due to the preparation method used. To date, surface areas typically in the range 2–7 m² g⁻¹ are readily achievable. Hence, although the intrinsic activity is higher than conventional catalysts, the overall reaction performance is not enhanced. In a future phase of this work, it will be important to devise methods of enhancing the surface area to ca. 30 m² g⁻¹ to gain the full advantage of the high intrinsic activity. In addition, the selectivity to maleic anhydride is somewhat lower than that observed for the current unpromoted conventional

VPA, VPO and VPD catalysts. This is considered to be due to non-optimal site isolation on the surface of the new amorphous vanadium phosphates and this can be addressed by modifying the surface V/P atomic ratio. However, the low selectivities may also be due to the level of Fe, Cr and Ni that are present acting as non-selective catalysts. It may also be important to prevent the reduction observed under *n*-butane oxidation conditions which is observed by the *in situ* NEXAFS investigation, and to stabilise the oxidation state close to V⁴⁺.

Using two complementary techniques to study the oxidation state of the vanadium in the bulk (by ³¹P spin echo mapping NMR) and at the surface (by NEXAFS) allows the structure-function analysis of the system, with respect to geometric and electronic structure, to be elucidated. In contrast to well ordered, crystalline systems where these properties are linked together, the amorphous microstructure may allow for independent control of geometry and electronic structure by introducing variable polyhedra lining as in glasses. A new functional model for this catalyst could be proposed with the vanadium phosphate providing a well-crystalline, stable, solid matrix (site isolation) for electronically variable disordered grains of a very similar chemical nature which carry the active sites. Hence, attempts will have to be made to independently control electronic and geometric structure by varying the gas phase chemical potential to allow assessments about the quality of a given material (based on testing conditions with fixed feed conditions) can be made.

The novel amorphous VPO material, prepared by precipitation with supercritical CO₂ as an antisolvent, demonstrates two clear differences with respect to the well studied crystalline vanadium phosphate catalysts derived from VOHPO₄·0.5H₂O. First, VPO_{SCPI} does not require an extensive pre-treatment time in the reactor. Stable catalytic performance is attained, and maintained for over 100 h, as soon as the catalyst reaches the required operating temperature. In contrast, catalysts derived from VOHPO₄·0.5H₂O always require 24–72 h in the microreactor under the reaction conditions to achieve stable catalytic performance (1,5,6,32). It is known that, during this period, the catalyst structure is established and the VOHPO₄·0.5H₂O topotactically transforms to (VO)₂P₂O₇, by either a direct pathway or an indirect route involving δ-VOPO₄ (6). Additionally, VOPO₄ phases are immediately formed and the active sites for the selective oxidation of *n*-butane to maleic anhydride are progressively generated on the surface of the crystallites with a specific dispersion of V⁵⁺ sites. Second, the amorphous VPO_{SCPI} is more active than catalysts derived from VOHPO₄·0.5H₂O on the basis of intrinsic activity (mol maleic anhydride produced/m²/h). Indeed, the VPO_{SCPI}-derived material remains amorphous during the reaction period and maintains this enhanced activity (Figure 2). This study, therefore demonstrates that a wholly amorphous VPO material can act as an effective catalyst and this is, perhaps, the most important observation from this study.

A number of previous studies (5,6,9–11,14–29) have suggested that amorphous VPO material can play an important role in the selective oxidation of *n*-butane. Many

studies have suggested that an amorphous overlayer on the crystalline VPO subsurface may be the active surface for this reaction (5,6,15,18,19,26-29). This has also been observed on related vanadium carbide catalysts for butane oxidation (21). It is generally acknowledged that the transformation from well crystalline VOHPO₄·0.5H₂O to the final active catalysts can involve the formation and transformation of amorphous material. This was first clearly demonstrated in our *in situ* laser Raman spectroscopy study of the pre-treatment step of the catalyst preparation (5). A key observation was that the selective oxidation of *n*-butane to maleic anhydride was only observed to commence following the formation of the amorphous vanadium phosphate material. The detailed combined microscopy and spectroscopy study of this pre-treatment stage also confirmed the formation of significant quantities of amorphous material (6).

Additional evidence in support of the proposal that the surface layer of the crystallites of vanadium phosphate is significantly different from the bulk is provided by the following observations: (a) X-ray photoelectron spectroscopy (1) consistently shows phosphorus enrichment in the surface layers (P:V ≥ 1.5) indicating that the surface is significantly different from the bulk structure of the crystallites. Fully crystalline structures of (VO)₂P₂O₇ and VOPO₄ would not be able to provide this degree of phosphorus enrichment. Furthermore, the phosphorus enrichment is enhanced during the transformation of the precursor VOHPO₄·0.5H₂O to the final catalyst; (b) catalysts prepared from VOHPO₄·0.5H₂O prepared by different routes are observed to give very different relative compositions of (VO)₂P₂O₇ and VOPO₄ phases, as determined by microscopy, diffraction and spectroscopy (32), but the catalysts will generally have very similar intrinsic activities for maleic anhydride production. This suggests that these different composition catalysts all exhibit the same active sites on the surface although the bulk structures are different, which is also supported in the present study by the similar NEXAFS of the fully amorphous and the crystalline catalyst; (c) in the present study, the assumed resonance position bond length relationship gives a high contribution of bond lengths which do not fit to the geometric structure of crystalline vanadyl pyrophosphate obtained by XRD; (d) the Co promoter for a vanadium phosphate catalyst, prepared using the VPO route, was found to phase segregate to, and stabilise, the amorphous material. Co was not found to be present (to the detectability limit of EDS) in the crystalline (VO)₂P₂O₇, yet the intrinsic activity of the Co-containing catalyst was enhanced by a factor of 3. This indicates that Co promotes the catalytic performance of the amorphous material derived from this preparation method. It is interesting to note that Co does not have this effect for the amorphous vanadium phosphate catalysts prepared using supercritical CO₂ as an antisolvent (29), at least at the concentration investigated in this study; (e) oxidation of (VO)₂P₂O₇ has been shown to enhance the selectivity to maleic anhydride and oxidise the surface of the catalyst (22,28). This oxidation treatment also correlates with an increase in the depth of the amorphous overlayer as observed on edge-on the (VO)₂P₂O₇ crystallites viewed using

very low illumination transmission electron microscopy (48).

In contrast, a number of researchers have concluded that the amorphous material is detrimental to catalyst performance (8-11,22) or that the amorphous material is a transient phase and that, following extensive reaction, only wholly crystalline VPO material is present (8-11). Gulianti *et al.* (9-11), in particular, conclude that the amorphous layer terminating the (200) planes of (VO)₂P₂O₇ observed in fresh catalysts was not observed in equilibrated catalysts obtained after many days of reaction. They conclude, in agreement with Albonetti *et al.* (16) and Ebner and Thompson (8) that the best catalytic performance is obtained for catalysts containing only (VO)₂P₂O₇ with the highest degree of stacking order. In addition, these researchers consider that VOPO₄ phases are detrimental to the catalyst performance. Indeed, Volta and co-workers (49) have shown that pure VOPO₄ phases are less selective for maleic anhydride than (VO)₂P₂O₇. However, a number of studies have shown that a combination of VOPO₄ phases, together with (VO)₂P₂O₇ can give enhanced catalyst performance (22,50,51). There remains, therefore, a considerable amount of debate concerning the nature of the active sites in vanadium phosphate catalysts, the preferred composition of the catalyst and the role of the amorphous material. One of the major problems preventing progress in this debate was that, in all these previous attempts to unravel the complexity of the role of the amorphous material, the catalysts all contained substantial quantities of crystalline phases in addition to the amorphous material.

In addition, all the evidence presented from detailed transmission electron microscopy studies concerning the presence or absence of amorphous overlayers has to be viewed with great care. We consider that the presence of an amorphous overlayer on (VO)₂P₂O₇, as noted in many studies (9-11,15,18,19,23,24), may result from a combination of one or more of the following processes: (i) exposure of the crystalline surfaces to the reactor feed producing amorphous material *in situ*; (ii) electron beam damage of the (VO)₂P₂O₇ crystallites (which are known to completely amorphise after 20-30 s under typical electron beam irradiation conditions in the microscope) and/or (iii) preferential electron beam sensitivity of a crystalline surface layer (e.g. VOPO₄ which is known to completely amorphise in a few seconds in the electron beam of the microscope) (33). It is therefore not possible, with transmission electron microscopy alone, to determine unequivocally whether the presence of a surface amorphous layer is simply an artefact due to beam damage or is, indeed, the genuine catalytically active phase. However, in the present study, the case is very clear. An amorphous VPO catalyst has been prepared which retains its amorphous nature throughout the reactor studies. Furthermore, the amorphous material requires no activation period and is more active, on a surface area basis, than the *crystalline* counterparts. Hence, the present study shows that amorphous VPO_{SCP1} materials are effective catalysts and require further study at this time. At this stage, it is not possible to determine if the amorphous VPO material, prepared using supercritical CO₂ as an antisolvent, is similar to either the

material observed during the transformation of VOHPO₄·0.5H₂O to (VO)₂P₂O₇ (5,6) or the amorphous layers observed supported on (VO)₂P₂O₇ crystallites (9-11) although the similarity of the V L₃-NEXAFS suggests a close relationship. On the basis of this study, we consider that the key matter for debate is not whether the catalysts derived from VOHPO₄·0.5H₂O comprise either wholly crystalline (VO)₂P₂O₇ or whether an amorphous layer supported on (VO)₂P₂O₇ is the active surface in these catalysts. Rather, it is crucial to determine the nature of the active site (e.g. V⁴⁺-V⁵⁺ dimers, isolated V⁵⁺ and V⁵⁺ microdomains as observed by ³¹P spin echo mapping) to prepare catalysts

with a high density of such sites whilst simultaneously maintaining site isolation to ensure high selectivity to maleic anhydride. Our study suggests that amorphous VPO catalysts may provide one route forward in identifying the optimal vanadium phosphate catalyst.

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