



Preparation of vanadium phosphate catalysts from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$: effect of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ preparation on catalyst performance

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Abstract

The preparation of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is described and discussed. Three samples of the dihydrate are prepared with different ageing times following the initial reflux of V_2O_5 with H_3PO_4 in water for 24 h. The materials were characterised using a combination of powder XRD, BET surface area measurement, laser Raman spectroscopy and scanning electron microscopy. A sample of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was isolated by immediate filtration of the reaction mixture and comprised flat oval crystallites with a broad size distribution between ca. 2 and 20 μm in diameter. Materials isolated following ageing of the initial reaction mixture (20 °C, 24 h) comprise square platelets again with a very broad size distribution. Using pyrophosphoric acid as the phosphorus source in place of phosphoric acid also affected the morphology of the $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. The dihydrates were reacted with isobutanol to form $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and these were transformed to $(\text{VO})_2\text{P}_2\text{O}_7$ by reaction with 1.7% *n*-butane in air at 400 °C. The most active catalyst was derived from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ prepared from ageing a reaction mixture following the removal of the first crop of crystals. The study shows that the method of preparation of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and, in particular, its morphology is of importance in the preparation of vanadium phosphate catalysts using the two stage method based on the reaction of the dihydrate with an alcohol to form the hemihydrate precursor.

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1. Introduction

The preparation of selective oxidation of *n*-butane continues to receive considerable research attention, and in particular the preparation of vanadium phosphate catalysts has been well studied [1–5]. The catalytic performance of vanadium phosphates depends on the method of preparation of the catalyst precursor, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ [6–22], and the reaction conditions utilised for the in situ activation in *n*-butane/air to form the final catalyst [6,7]. The active catalyst comprises $(\text{VO})_2\text{P}_2\text{O}_7$ in combination with some V^{5+} phosphates, typically α_{II} - and δ - VOPO_4 , and the transformation of the precursor to the final catalyst is topotactic. Hence, the precursor morphology is of importance in determining the eventual catalyst morphology and the performance following activation.

In view of the importance of the morphology of the catalyst precursor, there have been numerous studies concerned with catalyst preparation. In general, V_2O_5 is used as a source of vanadium, and H_3PO_4 is used as a source of phosphorus. Hence, a reducing agent is required to synthesise the V^{4+} precursor phase and a broad range of reducing agents and solvents have been employed [6–22]. Initial catalyst preparations [5,22] used water as solvent but most studies, in recent years, have concentrated on the use of alcohols as they can exhibit the dual role of solvent and reducing agent. In previous studies [14,23,24] we have shown that very active catalysts can be prepared using a two stage method based on $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. In particular, we have found that the alcohol used in the second step to reduce the $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ can control the morphology and the best results are obtained using primary alcohols. In this paper, we extend this earlier work and present a detailed study of the morphology and structure of vanadium phosphate catalysts prepared from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ obtained from different preparation methods.

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2. Experimental

2.1. Catalyst preparation

VOPO₄·2H₂O was prepared as follows. V₂O₅ (5.0 g, Strem) and H₃PO₄ (30 ml, 85%, Aldrich) were refluxed in water (120 ml) for 24 h. The yellow solid was recovered immediately without cooling by vacuum filtration, washed with hot water (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h). The material was then left in air at ambient temperature for 24 h to ensure full hydration. This material was denoted o-VPDi-A. The filtrate recovered from this method was allowed to stand at ambient temperature for 24 h during which time further yellow crystals were formed, these were recovered by vacuum filtration and washed and

treated as the previous sample. This material was denoted o-VPDi-B. A third sample of VOPO₄·2H₂O was prepared as follows. V₂O₅ (5.0 g, Strem) and H₃PO₄ (30 ml, 85%, Aldrich) were refluxed in water (120 ml) for 24 h. The mixture was cooled to ambient temperature (20 °C) and was allowed to stand for 24 h. The crystals formed were recovered by vacuum filtration, washed and treated as the previous samples. This material was denoted o-VPDi-C.

Vanadium phosphate catalyst hemihydrate precursors were prepared using the dihydrates as follows. The dihydrate (4 g) was refluxed with isobutanol (80 ml) for 21 h, and the resulting hemihydrate was recovered by filtration, dried in air (110 °C, 16 h). The hemihydrates were also refluxed in water (9 ml H₂O/g solid) for 2 h, filtered hot, and dried in air (110 °C, 16 h).

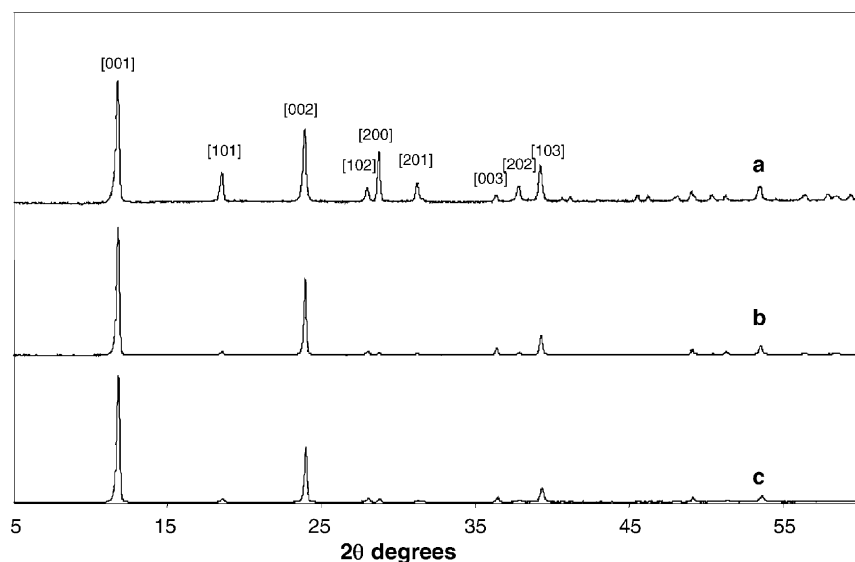


Fig. 1. Powder X-ray diffraction patterns of VOPO₄·2H₂O: (a) o-VPDi-A, (b) o-VPDi-B, (c) o-VPDi-C.

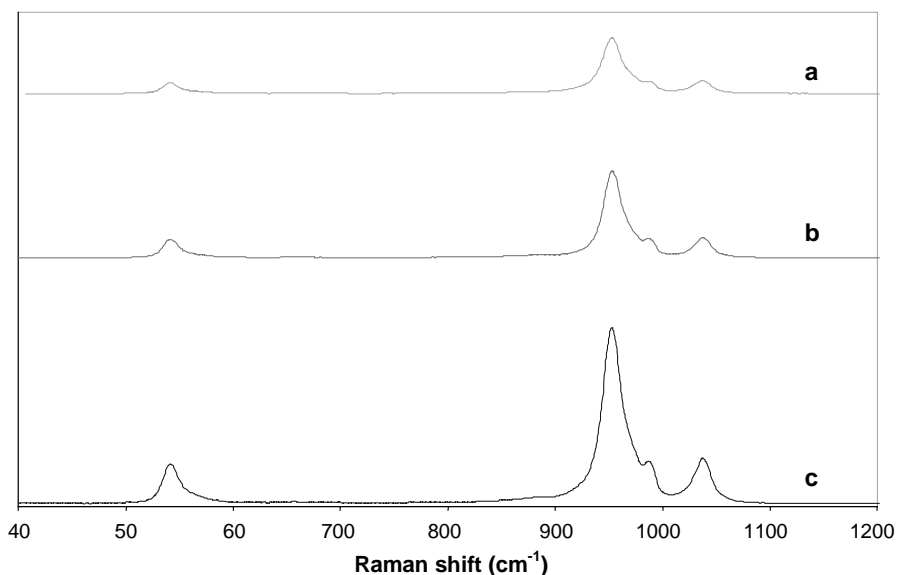


Fig. 2. Raman spectra of VOPO₄·2H₂O: (a) o-VPDi-A, (b) o-VPDi-B, (c) o-VPDi-C.

2.2. Catalyst testing and characterisation

The oxidation of *n*-butane was carried out in 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 1.7% *n*-butane in air. The products were then fed via heated lines to an on-line gas chromatograph for analysis. The reactor comprised a stainless steel tube with the catalyst held in place by plugs of quartz wool. A thermocouple was located in the centre of the catalyst bed and temperature control was typically ± 1 °C. Carbon mass balances of $\geq 97\%$ were typically observed. Catalyst samples were heated in situ (1.7% *n*-butane in air) at 400 °C by heating the sample from room temperature at a rate of 3 °C/min.

A number of techniques were used to characterise the catalyst structure. Powder X-ray diffraction (XRD) was performed using an Enraf Nonius FRS 590 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 ($\lambda = 514.532$ nm). Scanning electron microscopy (SEM) was performed on a Hitachi 326YO-N instrument operating at 20 kV.

3. Results and discussion

3.1. Catalyst precursor preparation and characterisation

o-VPDi-A, o-VPDi-B and O-VPDi-C were prepared as described and the yields based on the starting V₂O₅ are shown in Table 1. Overall the yields, as expected, are the same since the combined yield of o-VPDi-A (48%) and o-VPDi-B (24%) is equal to O-VPDi-C (72%). The powder X-ray diffraction patterns correspond to VOPO₄·2H₂O, with the dominant reflection at 11.8° indexed to the [001] plane (Fig. 1). The intensity of the [001] reflection relative to the other reflections (notably [002], [200] and [103])

increases in the order o-VPDi-A > o-VPDi-B > O-VPDi-C. This demonstrates that the morphology changes with increased ageing time of the dihydrate. The Raman spectra of the three materials (Fig. 2) are also consistent with VOPO₄·2H₂O as reported by Ben Abdelouahab et al. [13]. The main band at 953 cm⁻¹ is due to the symmetric stretch of P–O in the PO₄³⁻ tetrahedra and the bands at 987 cm⁻¹ and 1038 cm⁻¹ are due to the V–O and V–O–P stretching modes, respectively.

The morphology of the three different dihydrate samples was examined using scanning electron microscopy (Fig. 3). o-VPDi-A comprises flat oval crystallites with a broad size distribution between ca. 2 and 20 μm in diameter. Both o-VPDi-B and o-VPDi-C comprise square platelets again

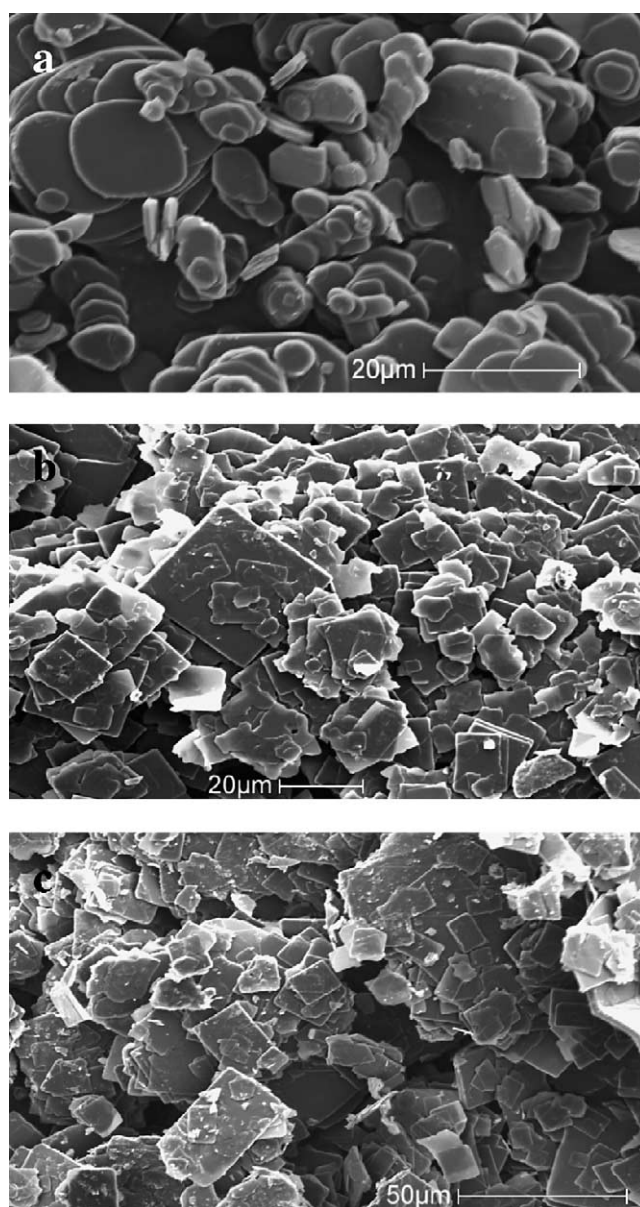


Fig. 3. Scanning electron micrographs of VOPO₄·2H₂O: (a) o-VPDi-A, (b) o-VPDi-B, (c) o-VPDi-C.

Table 1
Yields from preparation methods

Preparation method	Yield ^a (%)
o-VPDi-A	48
o-VPDi-B	24
o-VPDi-C	72
p-VPDi-A	37
p-VPDi-B	22
VPD-A	41
VPD-Aw	28
VPD-B	21
VPD-C	64
VPD-Cw	56

^a Yield based on V₂O₅.

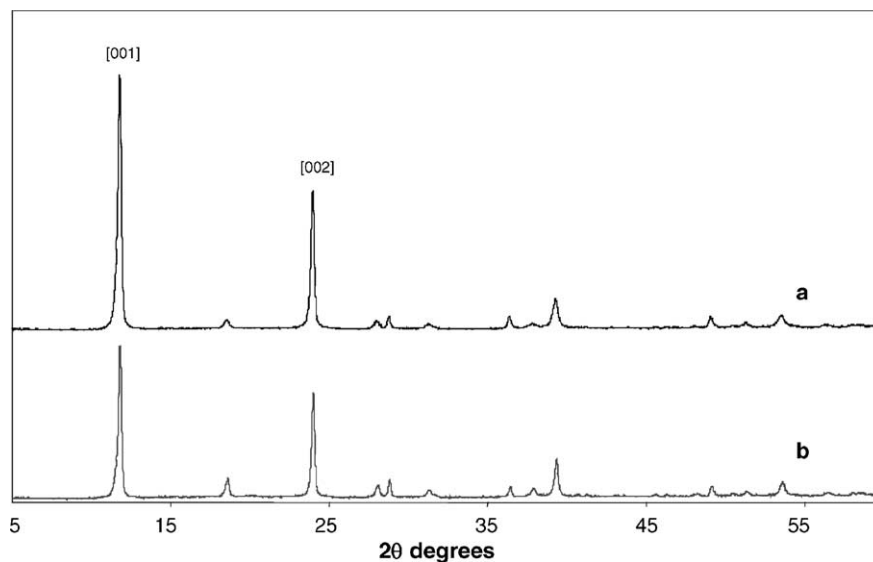


Fig. 4. Powder X-ray diffraction patterns of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$: (a) p-VPDi-A, (b) p-VPDi-B.

with very broad distribution, but o-VPDi-C has much larger crystallites. The morphologies are consistent with the powder X-ray diffraction data.

To determine if the phosphorus source was important two further dihydrate samples were prepared using pyrophosphoric acid in place of phosphoric acid using the methodology used to prepare o-VPDi-A and o-VPDi-B. We have previously shown that pyrophosphoric acid can be used to prepare high activity catalysts [25]. These materials are denoted p-VPDi-A and p-VPDi-B. The powder X-ray diffraction patterns (Fig. 4) are similar to those of o-VPDi-B (Fig. 1). The morphology (Fig. 5) shows that the material recovered immediately following the reflux period (p-VPDi-A) comprises irregular thin platelets, and consequently are very different from the material prepared in the same way using phosphoric acid. The material recovered from the filtrate after standing for 24 h (p-VPDi-B) comprises mainly flat square platelets and is very similar to the morphology of o-VPDi-B. These findings show that the source of phosphorus may be important with respect to the morphology of the dihydrate if it is recovered rapidly after synthesis.

The three dihydrate samples prepared from phosphoric acid were then reacted with isobutanol to form hemihydrates denoted VPD-A, VPD-B and VPD-C and the yields are given in Table 1. The powder X-ray diffraction patterns (Fig. 6) can be indexed to $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and the [00 1] reflection is most pronounced in VPD-A. The Raman spectra were all affected by fluorescence, but the main bands at 985, 1007, 1108, 1154 cm^{-1} of the hemihydrate are observed. The morphology of the materials was examined using scanning electron microscopy (Fig. 7) and all comprise rosettes of very thin platelets, with VPD-A having the smaller and more perfectly formed rosettes.

VPD-A and VPD-C were refluxed for 2 h and recovered by filtration to give materials denoted VPD-Aw and

VPD-Cw. No changes were observed in the powder X-ray diffraction pattern or the Raman spectra. The morphology of the hemihydrates as examined by scanning electron microscopy also did not reveal any changes to these materials due to the water reflux. The filtrates were evaporated to dryness and in many cases this gave a crystalline material which

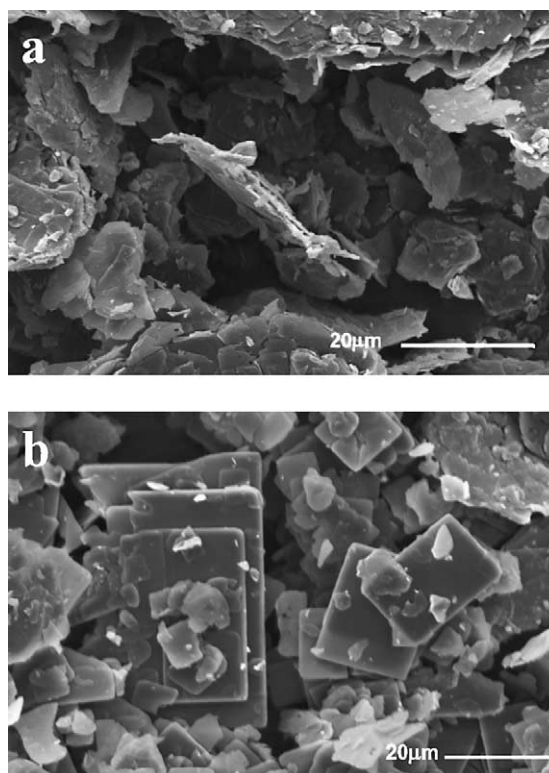


Fig. 5. Scanning electron micrographs of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$: (a) p-VPDi-A, (b) p-VPDi-B.

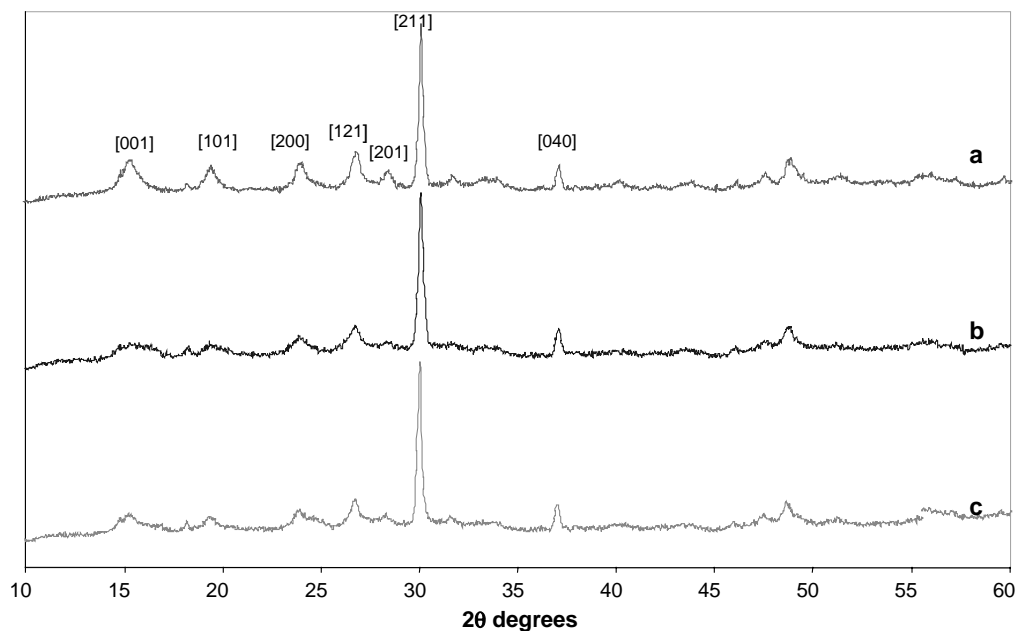


Fig. 6. Powder X-ray diffraction patterns of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$: (a) VPD-A, (b) VPD-B, (c) VPD-C.

was characterised as $\alpha_1\text{-VOPO}_4$ by powder X-ray diffraction and Raman spectroscopy. Sometimes a material amorphous to X-rays was also recovered, but by Raman spectroscopy this was also determined to be $\alpha_1\text{-VOPO}_4$.

3.2. Catalyst testing and characterisation

The five hemihydrate precursors were treated in situ in the laboratory microreactor with 1.7% *n*-butane in air at 400 °C.

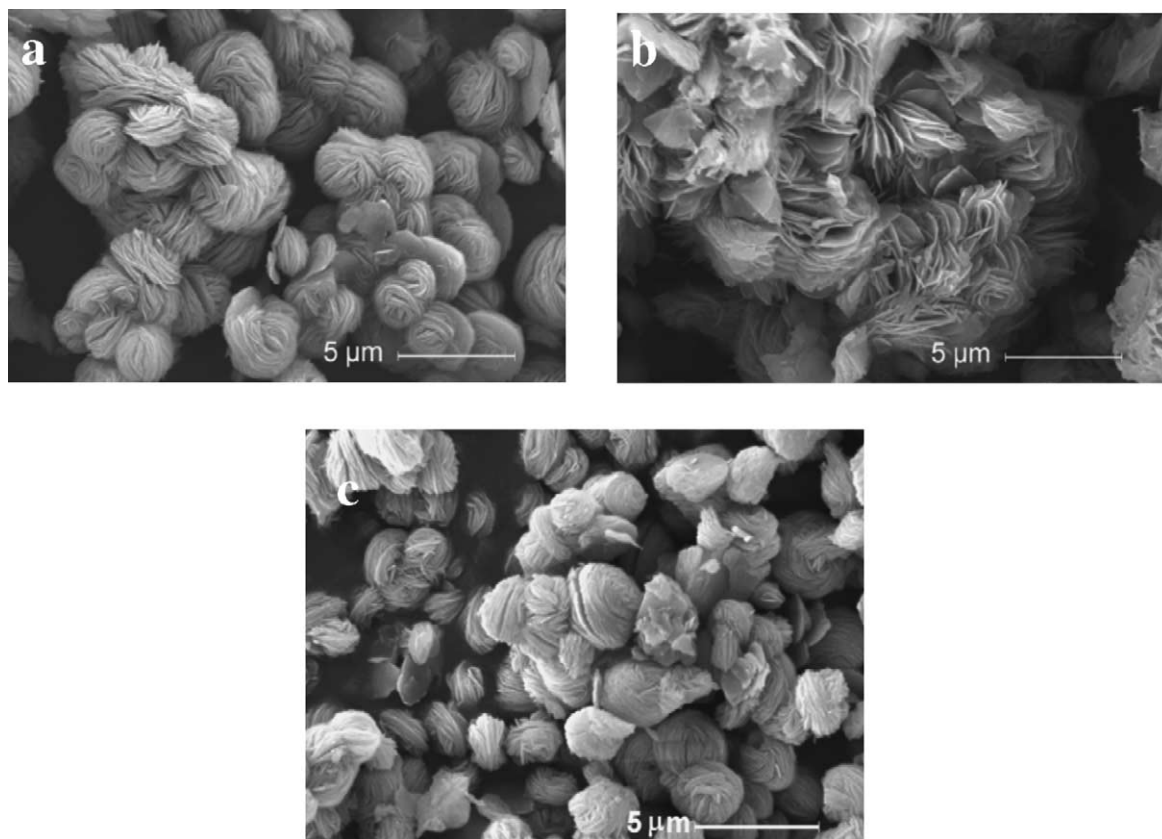


Fig. 7. Scanning electron micrographs of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$: (a) VPD-A, (b) VPD-B, (c) VPD-C.

Table 2
Catalyst performance of vanadium phosphate for the oxidation of *n*-butane^a

Catalyst precursor	Surface area	<i>n</i> -Butane conversion (%)	Product selectivity (%)			Intrinsic activity ^b (10 ⁻⁵ mol MA/m ² /h)	Specific activity ^c (10 ⁻⁴ mol MA/g/h)
			MA	CO	CO ₂		
VPD-A	17 ^d	49	85	8	7	4.43	7.52
VPD-Aw	21 ^d	71	72	15	13	3.89	8.16
VPD-B	17 ^d	71	72	15	13	5.04	8.57
VPD-C	13 ^d	36	69	17	14	4.44	5.77
VPD-Cw	7 ^d	37	63	23	14	3.20	4.79
α _I -VOPO ₄ ^e	13 ^f	12	71	17	13	2.53 ^g	3.29
Amorphous ^e	–	0	–	–	–	–	–

^a Reaction conditions: 400 °C, 1.7% *n*-butane in air, GHSV = 2500 h⁻¹.

^b Intrinsic activity: mol maleic anhydride formed/m² catalyst/h.

^c Specific activity: mol maleic anhydride formed/g catalyst/h.

^d Surface area of the catalyst following activation.

^e Materials derived from the filtrate after the water reflux of VPD-A and VPD-C.

^f Surface area of the material prior to catalyst testing.

^g Intrinsic activity based on surface area of the material prior to catalyst testing.

During this time the catalyst performance for the formation of maleic anhydride steadily improved. The catalyst performance data, when steady state had been obtained, are shown in Table 2 together with the surface areas of the catalysts. The most active catalysts for maleic anhydride synthesis were VPD-B and VPD-Aw which gave almost identical performance with surface areas of 17 and 21 m² g⁻¹. The water reflux step increased the surface area of VPD-A by 3 m² g⁻¹, leading to an increase in conversion and intrinsic activity. Surprisingly the surface area of VPD-C decreases after the treatment of water and the maleic anhydride selectivity is slightly decreased for VPD-Cw.

The powder X-ray diffraction patterns of the catalysts are shown in Fig. 8 and these can all be indexed to vanadyl pyrophosphate, (VO)₂P₂O₇, and the Raman spectra were consistent with this. Interestingly, the water washing treatment has distinctly different effects on VPD-A, prepared from the dihydrate recovered immediately after synthesis, and VPD-C

which was prepared from dihydrate that was aged for 24 h before isolation. For VPD-Aw the relative intensity of the [200] reflection relative to the [042] reflection is significantly enhanced, whereas in VPD-Cw the material is much less crystalline with respect to X-ray diffraction and, although the relative intensities of the [200] and [042] reflections are similar to VPD-Aw, the reflections are all very broad. This demonstrates that the morphology of the initial dihydrate can have significant effects on the subsequent morphology of the steady state activated catalyst, and in particular that water washing of precursors may not always be beneficial. The morphology effects are to be expected since the transformations of vanadium phosphates are topotactic and hence the initial morphology will have major consequences. The water washing effects require further comment, since for materials prepared in the one step aqueous or organic solvent routes the water refluxing of the precursor removes water soluble VO(H₂PO₄)₂ and this leads to a significant enhance-

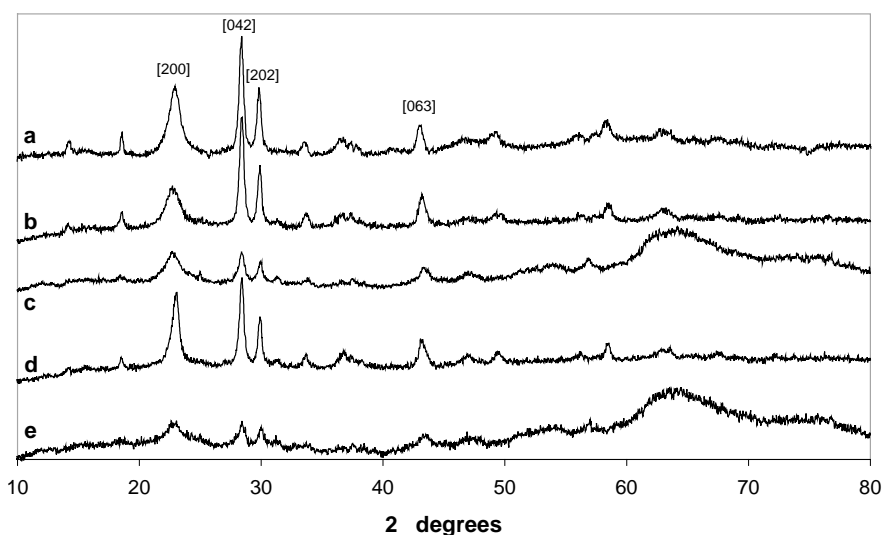


Fig. 8. Powder X-ray diffraction patterns of catalysts derived from precursors: (a) VPD-A, (b) VPD-B, (c) VPD-C, (d) VPD-Aw, (e) VPD-Cw.

ment in catalyst activity [5]. In the preparation of the hemihydrate using the one step procedures the initial P:V molar ratio is >1 . The high temperature water washing step therefore removes the excess phosphorus from the precursors. In the two step method based on the dihydrate the P:V molar ratio in the step that forms the precursor hemihydrate is unity. Consequently there is no excess phosphorus that requires removal. The high temperature water washing step in this case can significantly affect the crystallinity of the material and consequently the procedure has to be carried out with care.

The two materials recovered from the filtrate following the water washing procedure were also examined as catalysts (Table 2). The amorphous material was found to be inactive whereas the more crystalline material did display a low activity. After activation this material comprised α_I -VOPO₄ and α_{II} -VOPO₄.

In conclusion this study has shown that the manner in which the initial VOPO₄·2H₂O is prepared can have significant effects on its morphology. This subsequently affects the catalysts which are derived from the VOHPO₄·0.5H₂O formed from the reaction of the dihydrate with isobutanol.

Acknowledgements

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