Preparation of high surface area vanadium phosphate catalysts using water as solvent

Jose Antonio Lopez-Sanchez, Jonathan K. Bartley, Richard P. K. Wells,† Colin Rhodes and Graham J. Hutchings*

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK.
E-mail: hutch@cardiff.ac.uk

Received (in Montpellier, France) 29th April 2002, Accepted 8th August 2002
First published as an Advance Article on the web 17th October 2002

The synthesis of vanadium phosphorus oxide catalysts using water as solvent is described and discussed. The use of H_3PO_3 as a reducing agent is contrasted with aqueous hydrochloric acid. Using H_3PO_3 as a reducing agent for V_2O_5 at 145 °C for 72 h, together with H_3PO_4 or $H_4P_2O_7$ as the additional phosphorus source, is found to produce $VOHPO_4{\cdot}0.5H_2O$. Following activation in *n*-butane–air for 72 h, the catalysts derived from this method have surface areas (17–23 $m^2\ g^{-1}$) that are comparable to those prepared using a standard non-aqueous solvent method. The specific (mol maleic anhydride per g catalyst per h) and intrinsic (mol maleic anhydride $m^{-2}\ h^{-1}$) activities of the catalysts derived from using H_3PO_3 with water as solvent are also comparable to those for catalysts prepared using non-aqueous solvents. The activated catalysts comprise $(VO)_2P_2O_7$, together with α_{II}- and δ-$VOPO_4$. Refluxing the $VOHPO_4{\cdot}0.5H_2O$ catalyst precursors in water is found to decrease the crystallite size of the precursor, and this leads to higher area activated catalysts, but does not affect the specific or intrinsic activity significantly.

Vanadium phosphate catalysts for the selective oxidation of *n*-butane to maleic anhydride represent one of the most well studied heterogeneous catalysts.[1–5] In particular, there has been considerable interest in the synthesis of high activity, high surface area catalysts.[6–20] In general, the catalyst synthesis is a two-step procedure. Initially, a stable catalyst precursor, $VOHPO_4{\cdot}0.5H_2O$, is synthesised from the reaction of V_2O_5 with H_3PO_4 in the presence of a reducing agent and a solvent.[5,6] Subsequently, the precursor is transformed to the final catalyst, which comprises $(VO)_2P_2O_7$, together with α_{II}- and δ-$VOPO_4$ in an *n*-butane–air atmosphere at *ca.* 400 °C.[21,22] This transformation is topotactic[6,22–25] and, consequently, the morphology of the precursor is of critical importance in the establishment of a high area, high activity activated catalyst.

A large number of reducing agents and solvents have been utilised for the preparation of $VOHPO_4{\cdot}0.5HO$. Early methods[5] used water with aqueous hydrochloric acid as the reducing agent, denoted the VPA method. However, there were two disadvantages with this method; namely, only relatively low surface areas (1–3 $m^2\ g^{-1}$) could be achieved and, often, an impurity phase, $VO(H_2PO_4)_2$, was also formed.[26] Although the $VO(H_2PO_4)_2$ impurity can be readily removed by a water extraction step,[26] the surface areas of the extracted catalysts are still too low (*ca.* 4–9 $m^2\ g^{-1}$). In view of these disadvantages, the use of water as a solvent/reaction medium has not received recent attention. Most effort has been given to preparing catalysts in organic solvents and, in particular, alcohols have been used as both solvent and reducing agents.[6] Use of alcohols as reducing agents produces high activity catalysts with high surface areas ($\geqslant 20\ m^2\ g^{-1}$). Recently, we have shown[17] that the reaction of $VOPO_4{\cdot}2H_2O$ with alcohols also produces a high area catalyst and the morphology can be controlled by the choice of alcohol.[15]

Most recently, Guliants *et al.*[13–15] have described the synthesis of $VOHPO_3{\cdot}1.5H_2O$ using V_2O_5 with H_3PO_3 and anhydrous ethanol. In this reaction both the alcohol and the phosphorus source can act as reducing agents, and the resulting precursor produces a high activity catalyst for the oxidation of *n*-butane to maleic anhydride. In line with current environmental trends with respect to industrial manufacturing processes, it would be beneficial to design a synthesis for vanadium phosphorus oxide catalysts that either involved no solvent or used water as solvent. We have explored the use of water as solvent and, in this paper, we report the preparation of high area catalysts using water as solvent with H_3PO_3 as the reducing agent. In particular, with this methodology, we extend our earlier study[27] in which we explored the synthesis of vanadium phosphate catalysts at elevated temperatures using an autoclave.

Experimental

Catalyst preparation

Vanadium phosphate catalyst precursors were prepared using phosphorous acid as a reducing agent as follows. V_2O_5 (5.9 g, Strem, 99%), H_3PO_4 (2.2 g, Aldrich, 85 vol %) and H_3PO_3 (4.1 g, Aldrich, 99%) were mixed with distilled water (20 ml) and heated in an autoclave (145 °C, 72 h). Following the reaction, the solid produced was recovered by filtration, washed with cold distilled water (50 ml) and dried in air (120 °C, 16 h). This catalyst precursor, denoted VPO_{P1}, was then refluxed in distilled water for 2 h (20 ml H_2O per g solid). The resultant solid, denoted VPO_{P2}, was recovered by filtration, washed (50 ml H_2O) and dried in air (120 °C, 16 h). A similar preparation method was carried out using pyrophosphoric and phosphorous acid as follows. V_2O_5 (5.9 g, Strem, 99%), $H_4P_2O_7$ (1.703 g, Aldrich, 99%) and H_3PO_3 (4.1 g, Aldrich, 99%) were mixed with distilled water (20 ml) and

---

† Current address: Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, UK.

DOI: 10.1039/b203192m

Table 1 Catalyst performance data of vanadium phosphorus catalysts derived from H_3PO_3[a]

Catalyst precursor	Preparation method	Surface area/m^2 g^{-1} Precursor	Surface area/m^2 g^{-1} Catalyst	n-Butane conversion/%	Maleic anhydride selectivity/%	Specific activity/ 10^{-4} mol MA g^{-1} h^{-1}	Intrinsic activity/ 10^{-5} mol MA m^{-2} h^{-1}
VPO_{P1}	$V_2O_5 + H_3PO_4 + H_3PO_3$	5	11	26	46	1.87	1.70
VPO_{P2}	$V_2O_5 + H_3PO_4 + H_3PO_3$ + water reflux	11	17	62	56	5.43	3.19
VPO_{P3}	$V_2O_5 + H_4P_2O_7 + H_3PO_3$	6	8	17	50	1.33	1.66
VPO_{P4}	$V_2O_5 + H_4P_2O_7 + H_3PO_3$ + water reflux	13	23	63	57	5.61	2.44
VPA_1	$V_2O_5 + H_3PO_4 + HCl_{aq}$	1	1.5	4	45	0.281	1.88
VPA_2	$V_2O_5 + H_3PO_4 + HCl_{aq}$ + water reflux	3	4	11	45	0.773	1.93
VPD	$VOPO_4{\cdot}2H_2O$ + isobutanol + water reflux	18	22	65	58	5.89	2.68

[a] Reaction conditions 400 °C, 1.7% n-butane in air, GHSV = 2500 ml gas (ml catalyst)$^{-1}$ h^{-1}.

heated in an autoclave (145 °C, 72 h). Following the reaction, the solid produced, denoted VPO_{P3}, was recovered and treated as above to give the catalyst precursor denoted VPO_{P4}.

Two other precursors were prepared as comparative materials. A precursor was prepared according to the VPA method using water as a solvent.[17] V_2O_5 (6.06 g, Strem, 99%) was refluxed in aqueous HCl (37% by vol, BDH). H_3PO_4 (8.91 g, Aldrich, 85 vol %) was added to the solution and the mixture was refluxed for a further 2 h. The solution was partially evaporated and the solid formed was recovered by filtration and treated as described above. A precursor was prepared according to the VPD method with $VOPO_4{\cdot}2H_2O$ using isobutanol as solvent and reducing agents since this method typically gives high surface area vanadium phosphate precursors and catalysts.[17] V_2O_5 (11.8 g, Strem, 99%) and H_3PO_4 (15.5 g, Aldrich, 85 vol %) were refluxed in water (24 ml per g solid) for 8 h. The resulting $VOPO_4{\cdot}2H_2O$ was recovered by filtration and washed with a little water. Subsequently, $VOPO_4{\cdot}2H_2O$ (4 g) was refluxed in isobutanol (80 ml, Aldrich) for 21 h and the solid produced was recovered by filtration and treated as described above. The VPA and VPD precursors comprised $VOHPO_4{\cdot}0.5H_2O$ and characterisation by powder X-ray diffraction and laser Raman spectroscopy was consistent with previous published studies.[17,18]

These precursors (5 g) were subsequently refluxed in distilled water (100 ml) for 2 h. The solid was recovered by filtration when hot, washed with hot distilled water (50 ml) and dried in air (120 °C, 16 h). A summary of the preparation methods and precursor notation is included as part of Table 1.

Catalyst testing and characterisation

The oxidation of n-butane was carried out using a microreactor containing 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 1.7% 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. The catalyst precursor $VOHPO_4{\cdot}0.5H_2O$ was transformed to the final catalyst by heating in n-butane–air *in situ* in the reactor for typically 72 h (385 °C, 1000 h^{-1}) during which time the n-butane conversion and the maleic anhydride selectivity were observed to increase and stabilise.

A number of techniques were used to characterise the catalyst microstructure. Powder X-ray diffraction was performed using an Enraf Nonius FR590 X-ray generator with a Cu-Kα source fitted with an Inel CPS 120 hemispherical detector. Raman spectra were determined using a Renishaw Ramascope spectrograph fitted with a green Ar^+ laser (λ = 514.532 nm). Scanning electron microscopy analysis was carried out on a Hitachi S-2600-N-SEM. Surface areas of the materials were determined according to a multipoint BET procedure using N_2 adsorption carried out with a Micromeretics ASAP 2000 instrument.

Results and discussion

Catalyst precursor characterisation

A catalyst precursor was prepared using H_2PO_3 as the reducing agent with H_3PO_4 as the additional phosphorus source, this was denoted VPO_{P1}. Following treatment with hot water, the precursor was denoted VPO_{P2}. Precursors VPO_{P3} and VPO_{P4} were similarly prepared using pyrophosphoric acid ($H_4P_2O_7$) as the additional phosphorus source. The precursors were characterised using powder X-ray diffraction and laser Raman spectroscopy (Figs. 1 and 2) and were found to comprise solely $VOHPO_4{\cdot}0.5H_2O$ by these methods. Interestingly, no traces of $VO(H_2PO_4)_2$, an impurity noted to be readily formed under aqueous preparation conditions,[5] were observed to be present. A further experiment was carried out using H_2PO_3 and H_3PO_4 in which the product from the autoclave heating step was evaporated to dryness, without filtration. The material prepared was found to comprise $VOHPO_4{\cdot}0.5H_2O$, together with substantial quantities of $VO(H_2PO_4)_2$. However, following treatment with water under reflux for 2 h using the standard procedure, the precursor comprised only $VOHPO_4{\cdot}0.5H_2O$ and the powder X-ray diffraction patterns were indistinguishable from those for VPO_{P2} and VPO_{P4} shown in Figs. 1 and 2. It is therefore concluded

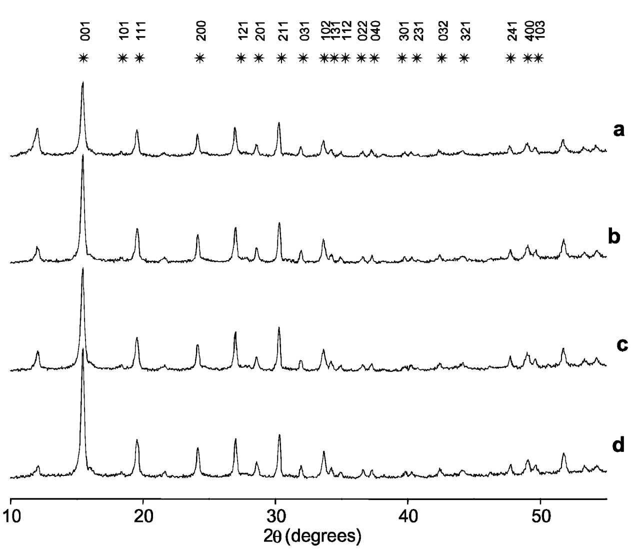

Fig. 1 Powder X-ray diffraction patterns of vanadium phosphate catalyst precursors prepared using the H_3PO_3 aqueous method; * indexes reflections for $VOHPO_4{\cdot}0.5H_2O$. Key: (a) VPO_{P1}; (b) VPO_{P2}; (c) VPO_{P3}; (d) VPO_{P4}.

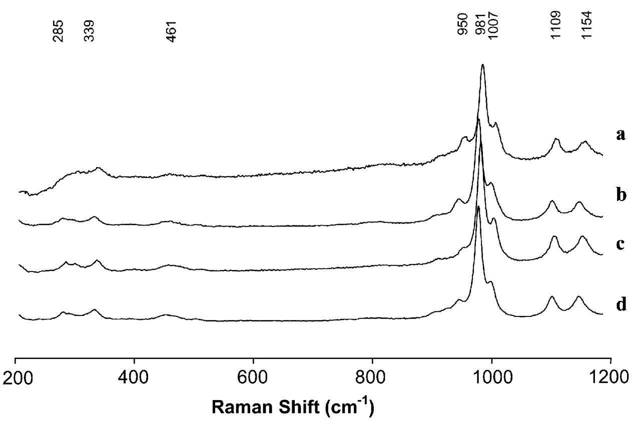

Fig. 2 Laser Raman spectra of vanadium phosphate catalyst precursors prepared using the H_3PO_3 aqueous method. Key: (a) VPO_{P1}; (b) VPO_{P2}; (c) VPO_{P3}; (d) VPO_{P4}.

that, when the precursor is recovered by filtration, following the autoclave stage of the preparation, the $VO(H_2PO_4)_2$ that forms during the preparation remains in solution. In previous studies[5,26] the water extraction of vanadium phosphate precursors has been viewed as essential for the removal of $VO(H_2PO_4)_2$ since, when this impurity is present, only low activity catalysts are subsequently produced with low surface areas. In the present case, when H_3PO_3 is used as a reducing agent, together with a filtration, no $VO(H_2PO_4)_2$ is formed. In this case, the water extraction procedure may have a different role and this was investigated subsequently.

It is possible that two other vanadium phosphates could also be formed during the autoclave preparation step. First, reduction of the V_2O_5 to a vanadium(III) species is possible, and this could form vanadium(III) phosphite, $VOHPO_3 \cdot 1.5H_2O$. This is observed in high yields when phosphorous acid, together with an alcohol, are reacted with V_2O_5 and H_3PO_4.[13] However, close inspection of the powder X-ray diffraction patterns and the laser Raman spectra do not reveal the presence of this material. Secondly, it is also possible that $VOPO_4 \cdot 2H_2O$ can be formed:

$$V_2O_5 + 2H_3PO_4 + H_2O \rightarrow 2VOPO_4 \cdot 2H_2O$$

However, the dihydrate is highly soluble in water and so would be expected to remain in solution during the preparation, in a similar manner to $VO(H_2PO_4)_2$, if it is formed. No evidence of the presence of $VOPO_4 \cdot 2H_2O$ as an impurity in the $VOHPO_4 \cdot 0.5H_2O$ is observed from the powder X-ray diffraction or laser Raman spectra (Figs. 1 and 2).

The four precursors were further characterised using scanning electron microscopy and the micrographs are shown in Fig. 3. It is apparent that the precursors comprise thin platelets with a broad range of crystallite sizes. It is clear that the precursors following the water reflux treatment, VPO_{P2} and VPO_{P4}, comprised much smaller crystallite sizes. This is consistent with the surface areas of these materials, which were determined by nitrogen adsorption according to the BET method (VPO_{P1}: 5 $m^2\ g^{-1}$; VPO_{P2}: 11 $m^2\ g^{-1}$; VPO_{P3}: 6 $m^2\ g^{-1}$; VPO_{P4}: 13 $m^2\ g^{-1}$). However, there are no significant differences observed in the powder X-ray diffraction patterns and laser Raman spectroscopy of these materials (Figs. 1 and 2). As noted above the water reflux step does not remove any phases from the precursors but it is clear that the crystallite size is decreased. It is possible that this is due to removal of traces of excess H_3PO_4 that could be occluded within the structure.

Catalyst testing and characterisation

The four catalyst precursors prepared with phosphoric acid as a reducing agent were treated *in situ* in the laboratory microreactor with 1.7% *n*-butane in air at 400 °C. During this time, the catalyst performance for the formation of maleic anhydride steadily improved (Fig. 4). The catalyst performance when the steady state was achieved is shown in Table 1, and data are also given for the materials prepared using the standard VPA and VPD methods. It is apparent that the catalysts derived from the H_2PO_3 aqueous method can produce high surface area and high activity catalysts, which have

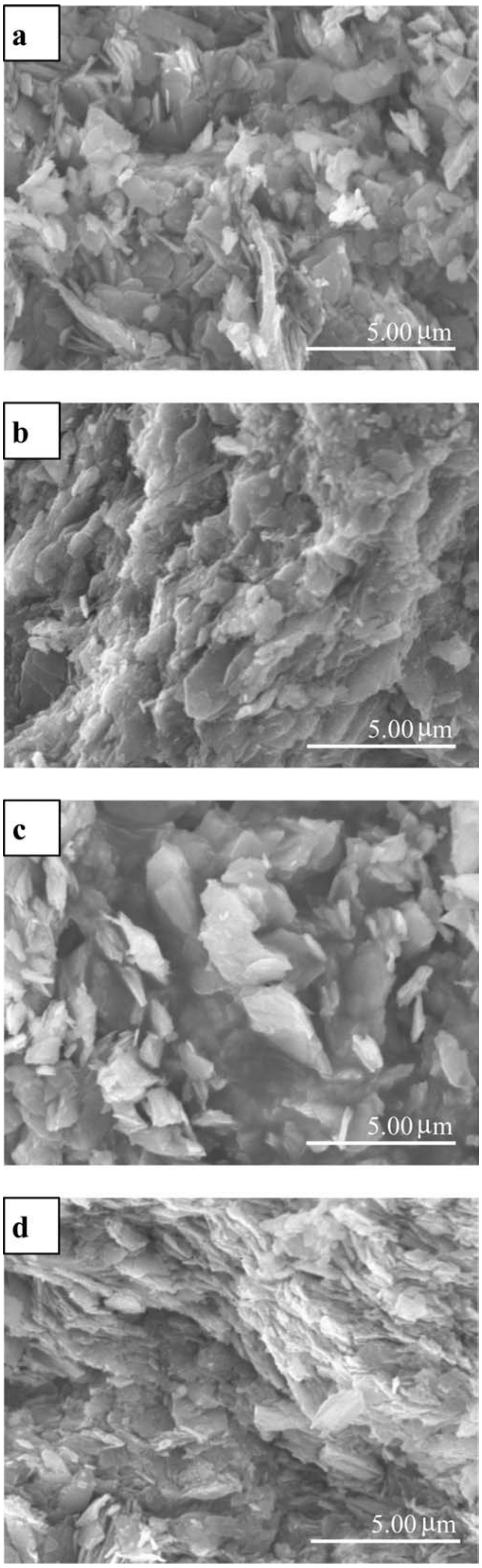

Fig. 3 Scanning electron micrographs of vanadium phosphate catalyst precursors prepared using the H_3PO_3 method: (a) VPO_{P1}; (b) VPO_{P2}; (c) VPO_{P3}; (d) VPO_{P4}.

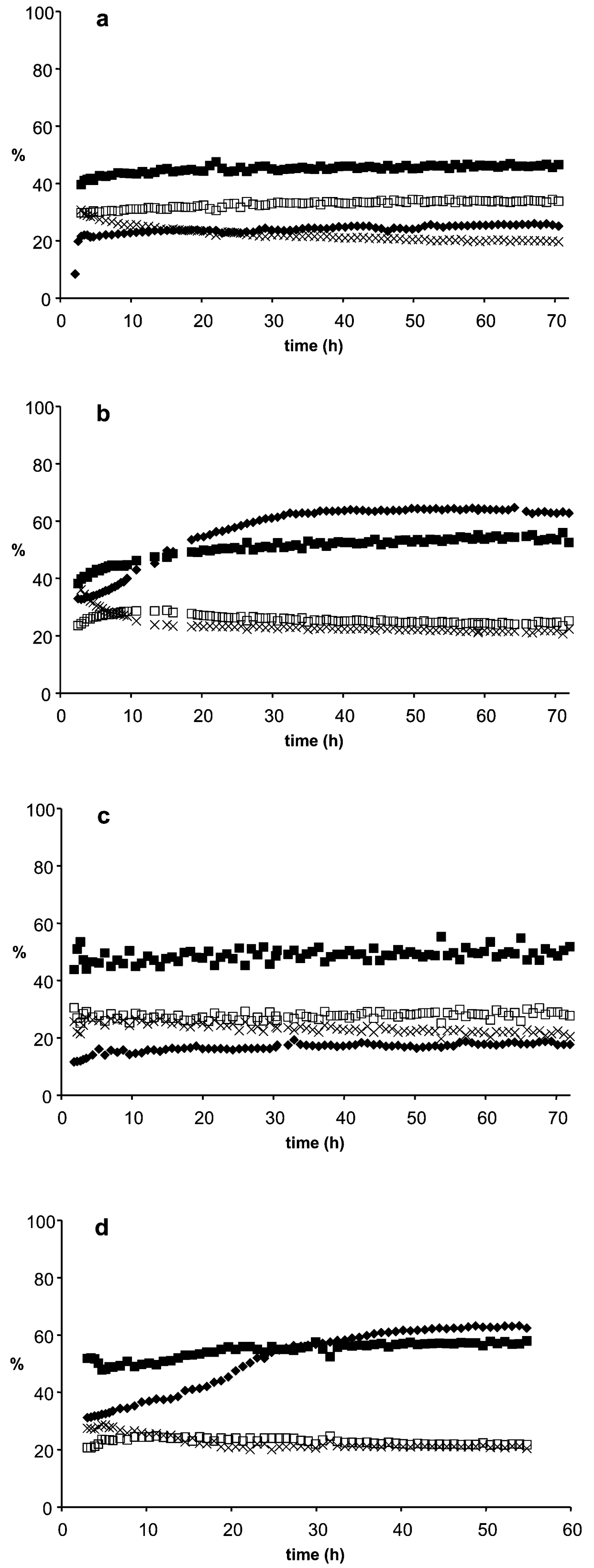

Fig. 4 Catalyst performance data for the catalysts prepared using the aqueous H_3PO_3 method. Reaction conditions: 1.7 vol % n-butane in air, 400 °C, 2500 ml gas (ml catalyst)$^{-1}$ h^{-1}. Key: (a) VPO_{P1}; (b) VPO_{P2}; (c) VPO_{P3}; (d) VPO_{P4}; ◆ n-butane conversion; ■ maleic anhydride selectivity; × CO_2 selectivity; □ CO selectivity.

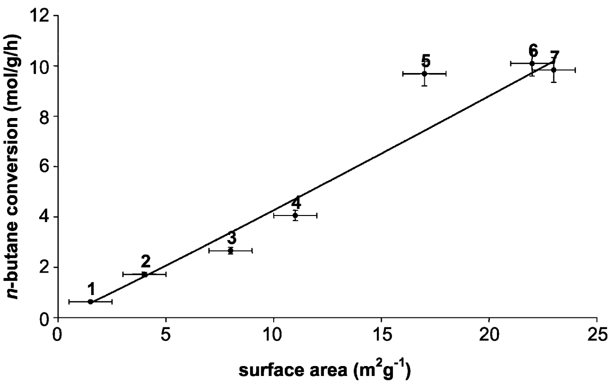

Fig. 5 Relationship between n-butane conversion (mol n-butane converted/g catalyst/h) and catalyst surface area. Key: 1 = VPA_1; 2 = VPA_2; 3 = VPO; 4 = VPO_{P1}; 5 = VPO_{P2}; 6 = VPO_{P3}; 7 = VPO_{P4}.

comparable performances with the catalysts prepared using an alcohol as solvent. When the H_3PO_3 aqueous method is contrasted with the standard aqueous HCl method of preparation, it is clear that the new H_3PO_3 method produces much higher surface area materials. This is considered to be due in part to the water washing step producing much smaller crystallites for these preparations where the impurity $VO(H_2PO_4)_2$ is absent. This difference is observed even when the VPA_1 precursor produced by partial solvent removal in the aqueous HCl method is refluxed in water to produce VPA_2. When the activity of the catalyst is normalised with respect to the surface area of the sample (intrinsic activity = mol maleic anhydride produced m^{-2} h^{-1}) all the samples show similar activities, indicating that the surface area of the catalyst is the most important parameter for these materials. This is further demonstrated by a plot of the specific n-butane conversion (mol n-butane converted per g catalyst per h) based on the mass of catalyst present (Fig. 5). It is clear that the specific activity is primarily dependent upon the catalyst surface area. It is possible that the material prepared using H_3PO_3 and H_3PO_4 may have a slightly higher specific activity than that expected from the correlation shown in Fig. 5.

Scanning electron microscopy of the catalyst following reaction (Fig. 6) shows the active catalyst comprises much smaller platelet-like crystallites than observed in the precursors (Fig. 3), which is consistent with the significant enhancement in surface area that is observed (Table 1).

Characterisation of the catalysts following reaction using powder X-ray diffraction (Fig. 7) and laser Raman spectroscopy (Fig. 8) showed the catalysts comprised a mixture of $(VO)_2P_2O_7$, together with δ-$VOPO_4$ and α_{II}-$VOPO_4$. Interestingly, the catalyst prepared using the aqueous phosphorous acid method with $H_4P_2O_7$ as the additional phosphorus source comprised mainly $(VO)_2P_2O_7$ with some α_{II}-$VOPO_4$. This material was similar to that prepared by the VPD method and it is noted that the two materials have similar surface areas and specific activities (Table 1). It is possible that the slightly enhanced specific activity observed with the catalyst derived from VPO_{P2} may be due to the combination of a higher proportion of V(v) phases in the bulk of the catalyst crystallites. This effect has been noted previously in vanadium phosphate catalysts prepared using water as solvent.[26] In addition, Coulston *et al.*[28] have recently shown that the concentration of V(v) sites in vanadium phosphate catalysts is of importance with respect to the synthesis of maleic anhydride and this may also be related to this effect.

Conclusions

Using H_3PO_3 as a reducing agent, high surface area vanadium phosphate catalyst precursors, comprising $VOHPO_4{\cdot}0.5H_2O$, and activated catalysts, comprising $(VO)_2P_2O_7$, α_{II}- and δ-$VOPO_4$, can be prepared using water as solvent. The specific

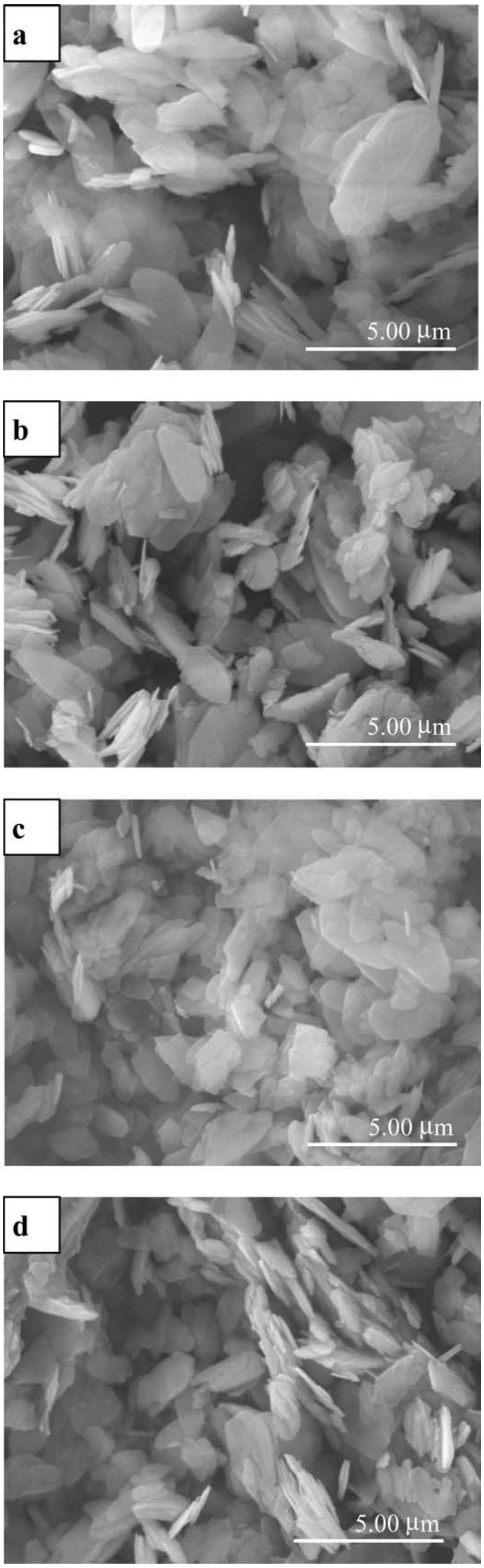

Fig. 6 Scanning electron micrographs of vanadium phosphate catalysts prepared using the H_3PO_3 aqueous method following reaction: (a) catalyst prepared from VPO_{P1}; (b) catalyst prepared from VPO_{P2}; (c) catalyst prepared from VPO_{P3}; (d) catalyst prepared from VPO_{P4}.

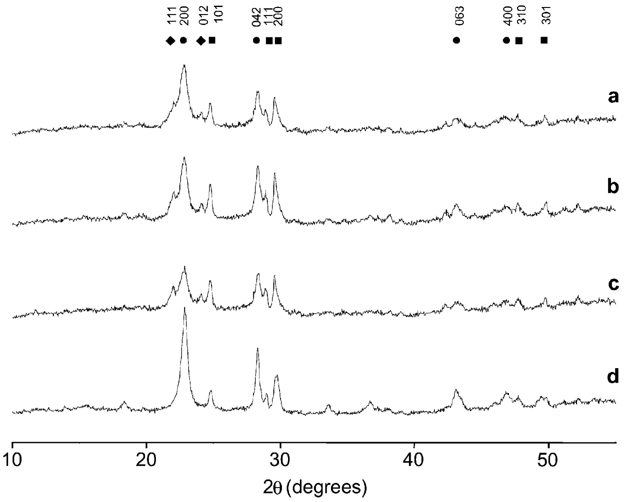

Fig. 7 Powder X-ray diffraction pattern of catalysts prepared using the H_3PO_3 aqueous method following reaction. Key: (a) VPO_{P1}; (b) VPO_{P2}; (c) VPO_{P3}; (d) VPO_{P4}; ● $(VO)_2P_2O_7$; ◆ δ-$VOPO_4$; ■ α_{II}-$VOPO_4$.

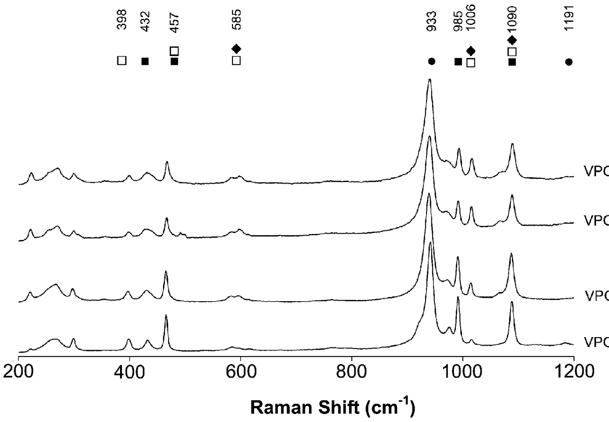

Fig. 8 Laser Raman spectra of vanadium phosphate catalysts prepared using the H_3PO_3 aqueous method following reaction. Key: (a) VPO_{P1}; (b) VPO_{P2}; (c) VPO_{P3}; (d) VPO_{P4}; ● $(VO)_2P_2O_7$; ◆ δ-$VOPO_4$; ■ α_{II}-$VOPO_4$; □ γ-$VOPO_4$.

and intrinsic activities of the activated catalysts produced using the H_3PO_3–H_2O method are comparable to those prepared using the standard non-aqueous/alcohol-based preparation methods. However, this method of preparation consistently yields high surface area materials (*ca.* 20 $m^2\ g^{-1}$) compared to previous water based methods that give only low surface area materials ($< 4\ m^2\ g^{-1}$). Previously, it has been widely considered that organic solvents are required for the synthesis of high area, high activity catalysts. The results of this study show that comparable materials can be produced using water as solvent. If the materials are recovered by filtration whilst hot no impurities [*e.g.*, $VOHPO_3 \cdot 1.5H_2O$, $VO(H_2PO_4)_2$, $VOPO_4 \cdot 2H_2O$] are formed. A subsequent water reflux treatment is observed to enhance the surface area of the activated catalyst, an effect primarily caused by the formation of smaller crystallites of the precursor.

Acknowledgement

We thank the EPSRC for financial support.

References

1 *Forum on Vanadium Pyrophosphate Catalysts*, ed. G. Centi, *Catal. Today*, 1994, **16**.
2 E. Bordes, *Catal. Today*, 1987, **1**, 499.

3 J. T. Gleaves, J. R. Ebner and T. C. Kuechler, *Catal. Rev. Sci. Eng.*, 1988, **30**, 49.

4 G. Centi, F. Trifiro, G. Busca, J. Ebner and J. Gleaves, *Faraday Discuss. Chem. Soc.*, 1989, **87**, 215.

5 G. J. Hutchings, *Appl. Catal.*, 1991, **72**, 1.

6 J. W. Johnson, D. C. Johnston, A. J. Jackson and J. F. Brody, *J. Am. Chem. Soc.*, 1984, **106**, 8123.

7 H. S. Horowitz, C. M. Blackstone, A. W. Sleight and G. Teufer, *Appl. Catal.*, 1988, **38**, 211.

8 E. W. Arnold and S. Sundaresan, *Appl. Catal.*, 1988, **41**, 457.

9 K. Ait-Lachgar, M. Abon and J. C. Volta, *J. Catal.*, 1997, **171**, 383.

10 E. A. Lombardo, C. A. Sanchez and L. M. Cornaglia, *Catal. Today*, 1992, **15**, 407.

11 F. Benabdelouahab, J. C. Volta and R. Olier, *J. Catal.*, 1994, **148**, 334.

12 I. J. Ellison, G. J. Hutchings, M. T. Sananes and J. C. Volta, *J. Chem. Soc., Chem. Commun.*, 1994, 1093.

13 V. V. Guliants, J. B. Benziger and S. Sundaresan, *Chem. Mater.*, 1995, **7**, 1485.

14 V. V. Guliants, J. B. Benziger, S. Sundaresan, I. E. Wachs and J. M. Jehng, *Chem. Mater.*, 1995, **7**, 1493.

15 V. V. Guliants, J. B. Benziger, S. Sundaresan, N. Yao and I. E. Wachs, *Catal. Lett.*, 1995, **32**, 379.

16 V. A. Zazhigalov, J. Haber, J. Storch, L. V. Bogutskaya and I. V. Bacherikova, *Appl. Catal.*, 1996, **135**, 155.

17 C. J. Kiely, A. Burrows, S. Sajip, G. J. Hutchings, M. T. Sananes, A. Tuel and J. C. Volta, *J. Catal.*, 1996, **162**, 31.

18 V. V. Guliants, J. B. Benziger, S. Sundaresan, I. E. Wachs, J. M. Jehng and J. E. Roberts, *Catal. Today*, 1996, **28**, 275.

19 J. Haber, V. A. Zazhigalov, J. Storch, L. V. Bogutskaya and I. V. Bacherikova, *Catal. Today*, 1997, **33**, 39.

20 W. H. Cheng and W. Wang, *Appl. Catal. A*, 1997, **156**, 57.

21 G. J. Hutchings, A. Desmartin Chomel, R. Olier and J. C. Volta, *Nature*, 1994, **368**, 41.

22 C. J. Kiely, A. Burrows, G. J. Hutchings, K. E. Bere, J. C. Volta, A. Tuel and M. Abon, *Faraday Discuss.*, 1996, **105**, 103.

23 E. Bordes, P. Courtine and J. W. Johnson, *J. Solid State Chem.*, 1984, **55**, 270.

24 C. C. Torardi and J. C. Calabrese, *Inorg. Chem.*, 1984, **23**, 1308.

25 E. Kesteman, M. Merzouki, B. Taouk, E. Bordes and R. Contractor, *Stud. Surf. Sci. Catal.*, 1995, **91**, 707.

26 G. J. Hutchings and R. Higgins, *J. Catal.*, 1996, **162**, 153.

27 J. K. Bartley, C. J. Kiely, R. P. K. Wells and G. J. Hutchings, *Catal. Lett.*, 2001, **72**, 99.

28 G. W. Coulston, S. R. Bare, H. Kung, K. Birkeland, G. K. Bethke, R. Harlow, N. Herron and P. L. Lee, *Science*, 1997, **275**, 191.