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Preparation of vanadium phosphate catalyst precursors using a high pressure method

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Abstract

The preparation of vanadium phosphate catalysts is known to be an important factor in determining their performance for the oxidation of butane to maleic anhydride. In this paper the preparation of catalyst precursors from V_2O_5 and H_3PO_4 using both aqueous hydrochloric acid and isobutanol as reducing agents are evaluated. In particular, the preparation of materials at higher temperatures using an autoclave method is described and compared with the materials prepared using the typical reflux methodology. The materials were characterised using a combination of powder XRD, BET surface area measurement, laser Raman spectroscopy and scanning electron microscopy. With the reflux method (1 bar pressure) both methods lead to the formation of $VOHPO_4{\cdot}0.5H_2O$. The aqueous hydrochloric acid method leads to the formation of $VO(H_2PO_4)_2$ as a minor impurity that is readily removed by water extraction. The high temperature autoclave route gives significant differences. The aqueous hydrochloric acid route surprisingly does not give V^{4+} phases but gives a mixture of hydrated $VOPO_4{\cdot}xH_2O$ phases. In contrast the isobutanol method at higher temperature and pressure gave $VOHPO_4{\cdot}0.5H_2O$ as expected. However, for both methods the use of the higher temperature and higher pressure led to lower surface area materials being formed and consequently this will limit the usefulness of this methodology with these reducing agents.

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1. Introduction

The selective oxidation of *n*-butane continues to receive considerable research attention [1–5]. In this respect vanadium phosphate catalysts have been extensively investigated and to date they represent the sole example of a commercial catalyst for the selective oxidation of an alkane. In particular, the group of Trifirò and co-workers [4,6–12] have made significant contributions to our understanding of these complex catalysts.

The catalytic performance of vanadium phosphates depends on the method of preparation of the catalyst precursor, $VOHPO_4{\cdot}0.5H_2O$ [12–24], and the reaction conditions utilised for the in situ activation in *n*-butane/air to form the final catalyst [12,13]. The active catalyst comprises $(VO)_2P_2O_7$ 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 preparation route and precursor morphology is of importance in determining the eventual catalyst morphology and the performance following activation.

In general, for the preparation of $VOHPO_4{\cdot}0.5H_2O$, 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 [12–24]. Early studies tended to use water as solvent and in this case hydrochloric acid was utilised as reducing agent. This method prepares low area materials that have $VO(HPO_4)_2$ as an impurity. A major innovation was the introduction of an alcohol, typically isobutanol, as both the solvent and the

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reducing agent [15], and this method tends to give much higher surface area materials without the presence of impurities.

Vanadium phosphates present a rich chemistry for the preparative chemist and a large number of specific compounds can be readily formed. Although many materials used as catalysts are prepared using ambient pressure methods where V_2O_5 and H_3PO_4 as starting reagents are refluxed with a reducing agent, there have been a great number of studies that have explored the use of higher pressures in the synthesis of vanadium phosphates [25–29]. In all these methods, organic structure directing agents are used and these are often incorporated or intercalated into the final structure. Indeed the use of surfactants as additives has been investigated under mild conditions for the synthesis of vanadium phosphates and ordered mesostructured vanadium phosphates have been reported [30,31], and the use of alcohols to exfoliate the laminar structure of vanadium phosphates is now receiving attention [32]. Recently, we have shown that water can be used as a solvent to prepare high area catalysts using H_3PO_3 or V_2O_4 as reagents and using higher temperatures and pressures for the preparation using an autoclave method but, in the absence of any organic structure directing reagents [24]. To date the aqueous hydrochloric acid and isobutanol methods of vanadium phosphate preparation methods have only been explored using ambient pressure reflux methods. In this paper we investigate the use of the higher temperature/pressure autoclave method with these two reducing agents and compare the materials synthesised with the materials prepared using the standard ambient pressure reflux method.

2. Experimental

2.1. Catalyst preparation

Two standard ambient pressure preparations were carried out as follows:

- *Standard aqueous method.* V_2O_5 (6.06 g, Strem) was refluxed in aqueous hydrochloric acid (35%, 79 ml) for 2 h. H_3PO_4 (8.91 g, 85%, Aldrich) was added and the solution was refluxed for an additional 2 h. The mixture was evaporated to dryness and the material was denoted VPA. VPA was refluxed in water (9 ml H_2O/g solid) for 2 h, filtered hot, and dried in air (110 °C, 16 h) to give a material denoted VPAw.
- *Standard isobutanol method.* V_2O_5 (11.8 g, Strem) and H_3PO_4 (30 ml, 85%, Aldrich) were refluxed for 16 h. The light blue solid was recovered by filtration and the material was denoted VPO. VPO was refluxed in water (9 ml H_2O/g solid) for 2 h, filtered hot, and dried in air (110 °C, 16 h) to give a material denoted VPOw.
- *Standard high temperature autoclave method.* Mixtures of V_2O_5, H_3PO_4 and aqueous hydrochloric acid or V_2O_5, H_3PO_4 and isobutanol in the amounts given above were sealed into a pressure vessel and heated to 145 °C for a range of reaction times. The solids were recovered either by filtration or by evaporation to dryness as described above and denoted HP-VPA and HP-VPO.

2.2. Catalyst characterisation

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 Kα source fitted with an Inel CPS 120 hemispherical detector. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics ASAP 2000 instrument. Raman spectra were obtained using a Renishaw Ramanscope Spectrograph fitted with a green Ar^+ laser ($\lambda = 514.532$ nm). 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 using the ambient pressure reflux method

VPA was prepared as described and the powder X-ray diffraction pattern (Fig. 1a) and the reflections could all be indexed to $VOHPO_4{\cdot}0.5H_2O$, with the dominant reflections at $d = 5.739$ Å indexed to the [0 0 1] plane and $d = 2.934$ Å indexed to the [2 1 1] plane. This is standard for materials made by this method [20]. In particular, there is no evidence of $VO(H_2PO_4)_2$ as an impurity using this characterisation technique. However, this would be unusual for this method [5] and consequently we investigated the material using laser Raman spectroscopy (Fig. 2a) since this method is particularly sensitive to different vanadium phosphate phases and can be useful in detecting the presence of non-crystalline materials. The main Raman bands could all

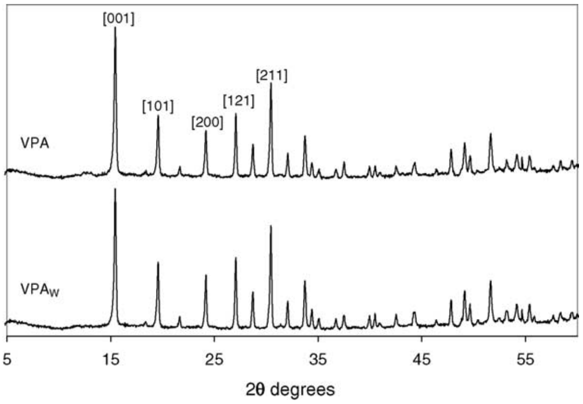

Fig. 1. Powder X-ray diffraction patterns: (a) VPA and (b) VPAw.

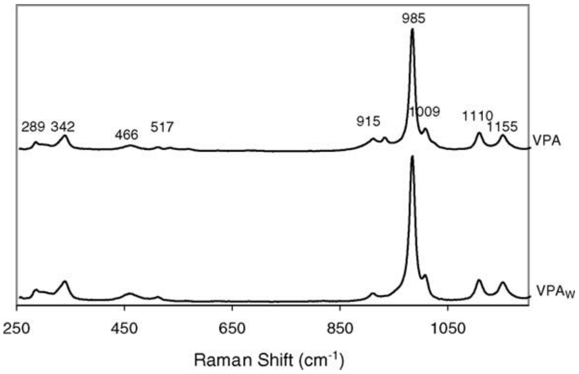

Fig. 2. Laser Raman spectra: (a) VPA and (b) VPAw.

be assigned to $VOHPO_4 \cdot 0.5H_2O$, however, there are additional bands at 935, 569 and 536 cm^{-1} which can be assigned to $VO(H_2PO_4)_2$ showing that this phase is present, as expected. VPA was then refluxed in water to prepare VPAw and the powder X-ray diffraction pattern and laser Raman spectrum are shown in Figs. 1b and 2b, respectively. The powder X-ray diffraction pattern of VPA and VPAw are almost identical except the reflections for the [1 0 1], [1 2 1] and [2 1 1] planes are enhanced relative to that of the most intense reflection of the [0 0 1] plane by ca. 15%. In the laser Raman spectrum of VPAw the bands assigned to $VO(H_2PO_4)_2$ are absent confirming that the water reflux treatment had removed this soluble vanadium phosphate from the precursor. Scanning electron microscopy (Fig. 3) of the two materials shows them to have very similar morphology, in agreement with the powder X-ray diffraction data, and they comprise small platelets ca. 1–4 μm in diameter and 0.2–1 μm in thickness. The water reflux treatment does not significantly affect the morphology although VPAw does contain some smaller crystallites. The BET surface areas of VPA and VPAw were determined to be 1 and 2 $m^2 g^{-1}$, respectively, and these are also consistent with the micrographs.

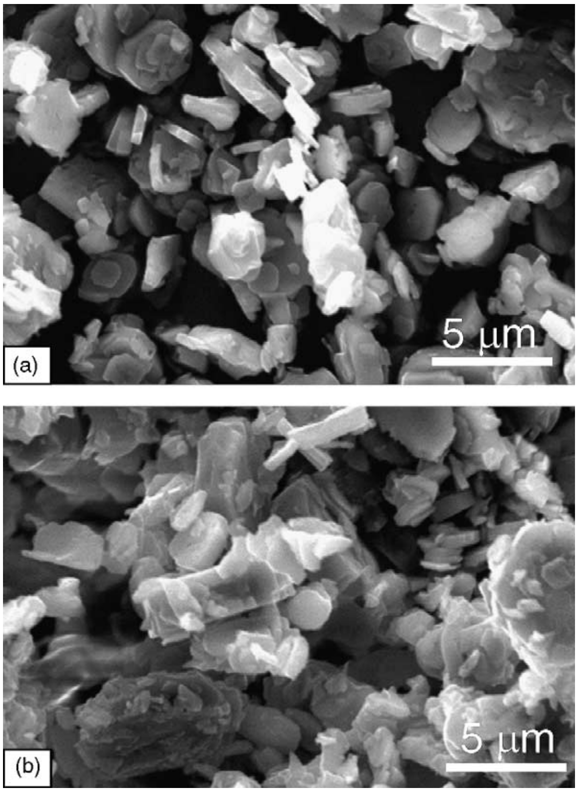

Fig. 3. Scanning electron micrographs: (a) VPA and (b) VPAw.

VPO was prepared as described and the powder X-ray diffraction pattern (Fig. 4a) and the reflections could all be indexed to $VOHPO_4 \cdot 0.5H_2O$, with the dominant reflections at $d = 5.728$ Å indexed to the [0 0 1] plane and $d = 2.932$ Å indexed to the [2 1 1] plane. This pattern is similar to other materials made by this method [20]. In particular, as for VPA, there is no evidence of $VO(H_2PO_4)_2$ as an impurity. However, this impurity is not often observed for this method [5]. This was confirmed using laser Raman spectroscopy and although the spectrum exhibited fluorescence, due to the occlusion of isobutanol within the VPO crystallites, since all the Raman bands could be assigned to $VOHPO_4 \cdot 0.5H_2O$. VPO was then refluxed in water to form VPOw. The powder X-ray diffraction patterns of VPO and VPOw (Fig. 4b) are almost identical except that following the water reflux step, the reflection for the [0 0 1] plane is enhanced in intensity relative to the intensities of the [1 0 1], [1 2 1] and [2 1 1] planes, which is opposite to the effect observed with water refluxing VPA. Scanning electron microscopy (Fig. 5) of the two materials shows them to have very similar rosette morphology, often observed for this method [20] and the water reflux treatment does not significantly affect the morphology. The BET surface areas of VPO and VPOw were determined to be 9 and 11 $m^2 g^{-1}$, respectively, and these are also consistent with the micrographs.

3.2. Catalyst precursor preparation and characterisation using the high pressure autoclave method

HP-VPA compounds were prepared by reacting V_2O_5, H_3PO_4 and aqueous hydrochloric acid in a sealed autoclave at 145 °C. Three materials were prepared by heating for 3, 6 and 16 h and the powder X-ray diffraction patterns are

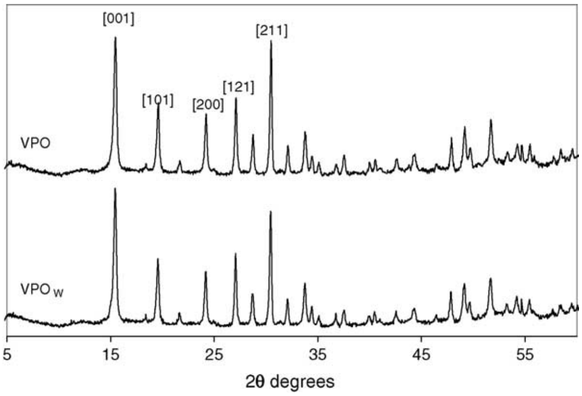

Fig. 4. Powder X-ray diffraction patterns: (a) VPO and (b) VPOw.

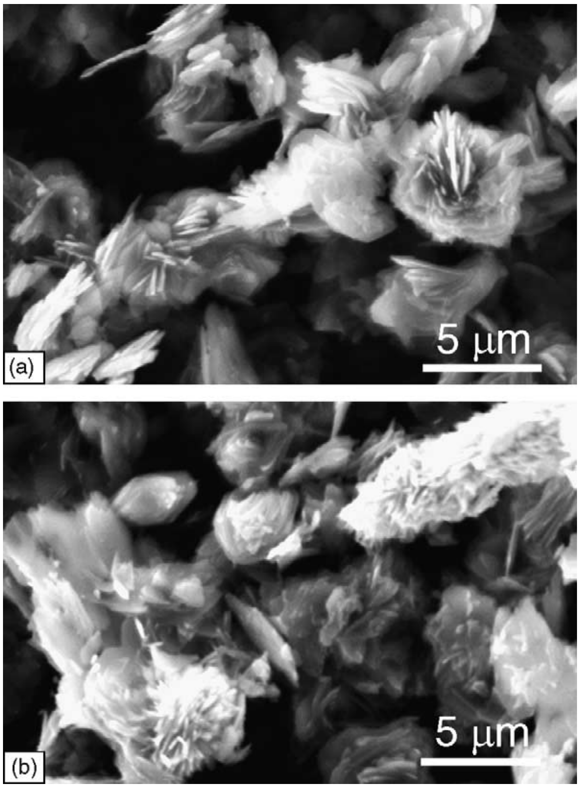

Fig. 5. Scanning electron micrographs: (a) VPO and (b) VPOw.

shown in Fig. 6. None of the reflections index to the hemihydrate $VOHPO_4 \cdot 0.5H_2O$ or $VO(H_2PO_4)_2$ which is a surprising observation. It is clear that the material changes as the reaction time is increased and the pattern is relatively simple and most lines can be indexed to $VOPO_4 \cdot 2H_2O$ and related hydrated $VOPO_4$ phases. This was confirmed by the laser Raman spectra (Fig. 7) which show the materials to be very similar to the Raman spectrum of $VOPO_4 \cdot 2H_2O$. It is therefore clear that reduction to V^{4+} had not occurred during this preparation method. The surface areas of the three materials were all ca. 1 $m^2 g^{-1}$.

HP-VPO compounds were prepared by reacting V_2O_5, H_3PO_4 and isobutanol in a sealed autoclave at 145 °C. Three materials were prepared by heating for 9, 16 and 72 h and the powder X-ray diffraction patterns are shown in Fig. 8. All the reflections index to the hemihydrate $VOHPO_4 \cdot 0.5H_2O$ and $VO(H_2PO_4)_2$ was not observed. As the reaction time increased the intensity of the reflection at $d = 5.7$ Å, assigned to the [0 0 1] plane of the hemihydrate, increases in intensity relative to the other reflections. Scanning electron microscopy (Fig. 9) shows that the material after 72 h reaction comprises small platelets with some rosette formation. Water reflux of HP-VPO-72 leads to a loss of the rosette morphology (Fig. 9) and the intensity of the [0 0 1] reflection is further enhanced (Fig. 8). The effect of the water reflux process is therefore very different from that observed for the material prepared using the ambient pressure reflux method. Interestingly, the surface areas of the materials decrease with increasing reaction time at pressure (HP-VPO-6 = 8 $m^2 g^{-1}$, HP-VPO-16 = 3 $m^2 g^{-1}$, and HP-VPO-72 = 2 $m^2 g^{-1}$). The water reflux step does not enhance the surface area of the material.

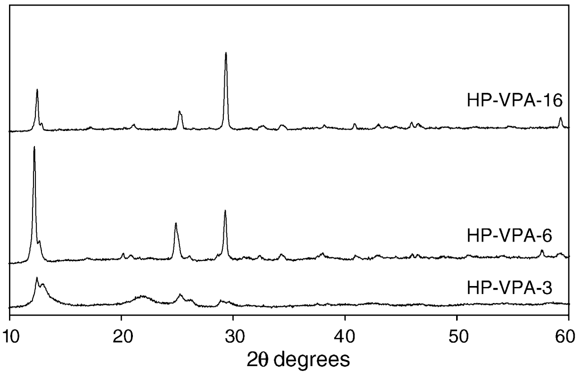

Fig. 6. Powder X-ray diffraction patterns of HP-VPA materials.

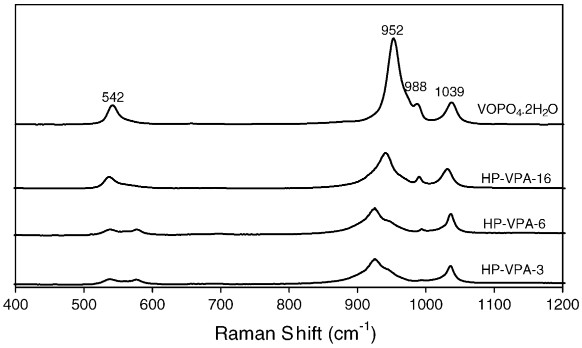

Fig. 7. Laser Raman spectra of HP-VPA materials compared with $VOPO_4 \cdot 2H_2O$.

3.3. Comparison of the ambient pressure and high pressure methods for preparing vanadium phosphate precursors

There appear to be two clear differences between the two methodologies. For the method preparing VPO type materials, both the ambient pressure reflux method and the autoclave method lead to the preparation of $VOHPO_4 \cdot 0.5H_2O$. However, the morphology is affected by the preparation method. At elevated pressure the intensity of the [0 0 1] reflection is enhanced and the surface area of the

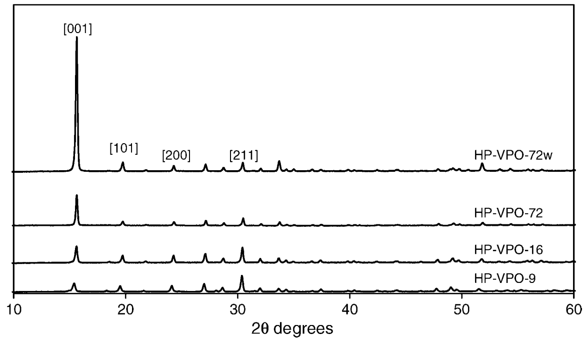

Fig. 8. Powder X-ray diffraction patterns HP-VPO materials compared with $VOPO_4 \cdot 2H_2O$.

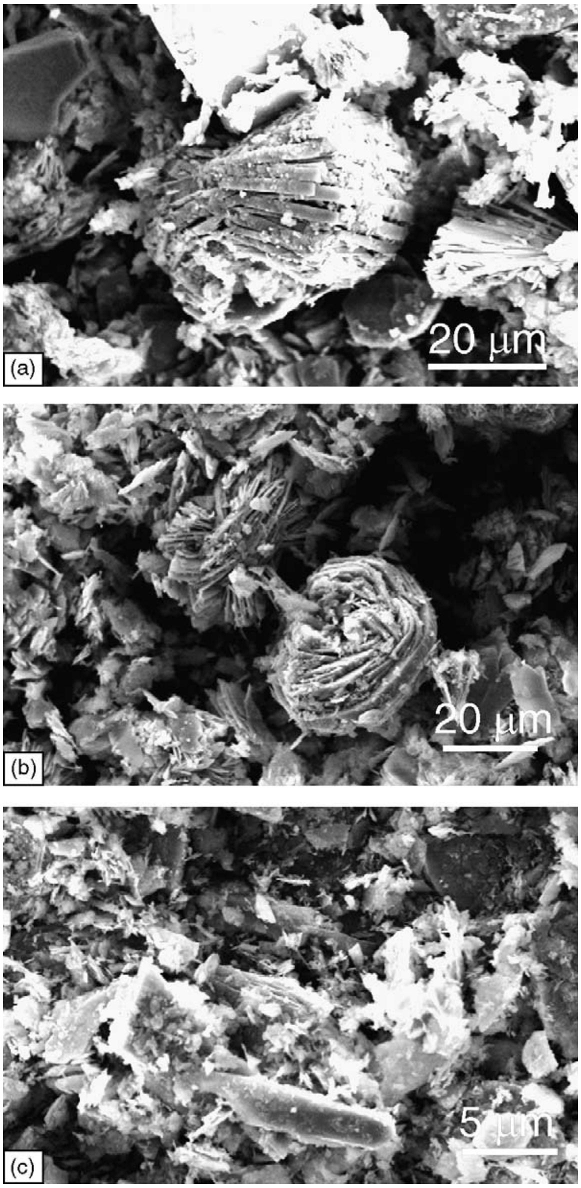

Fig. 9. Scanning electron micrographs: (a) HP-VPO-9, (b) HP-VPO-72 and (c) HP-VPO-72w.

hemihydrate is significantly decreased and only some rosette morphology is observed. It is apparent that at higher pressure the hemihydrate surface area does not develop and consequently with the method, using an alcohol as the reducing agent, is not advantaged by using increased temperatures and pressures. This is in direct contrast to our recent study using aqueous methods in an autoclave at 145 °C starting with V_2O_5 with H_3PO_3 as reducing agent or starting with V_2O_4 reacted with H_3PO_4 [24]. In that study the aqueous methods gave very high surface areas ≥ 20 m^2 g^{-1} for the hemihydrate precursors. It is clear that this is not replicated when water is replaced by an alcohol. If the alcohol is not added to the autoclave, i.e. V_2O_5 reacted only with H_3PO_4 at 145 °C in an autoclave for 16 h, then a low area (3 m^2 g^{-1}) V^{5+} vanadium phosphate is obtained [33]. From this it is clear that addition of the alcohol enable the reduction of V^{5+} to V^{4+} to occur but its presence has no effect on the surface area since this remains at 3 m^2 g^{-1} for the material prepared for 16 h reaction. This is a very interesting observation since it has often been considered that the high areas associated with the use of alcohols is solely related to the occlusion of the alcohol within the layer structure of the hemihydrate, which when it is removed on drying leads to higher area exfoliated crystallites. Indeed, recent studies using alcohols to exfoliate the laminar structure of vanadium phosphates have been shown to lead to increased surface areas [32]. The present study shows that the origin of the higher surface area is more complex in the standard preparation methods.

The second observation that requires comment is that the VPA methodology at first sight does not lead to the formation of $VOHPO_4{\cdot}0.5H_2O$. However, the ambient pressure VPA method is carried out in two steps. First, the V_2O_5 is reacted with aqueous hydrochloric acid and this forms V^{4+} compound $VOCl_2$ which is then reacted in the second step with H_3PO_4. In the high pressure HP-VPA method both steps have been combined and it is apparent that when H_3PO_4 is present the reduction of V^{5+} to V^{4+} does not occur, even when the reaction is carried out at the elevated temperature/pressure for significantly longer times (16 h) compared to the ambient reflux period (4 h). To confirm this a one step experiment was carried out using the ambient pressure reflux method in which V_2O_5, H_3PO_4 and aqueous hydrochloric acid were refluxed together for 16 h. This resulted in the formation of a green solid which was a mixture of hydrated forms of $VOPO_4{\cdot}xH_2O$. In addition, we have previously shown that the reaction of V_2O_4 with H_3PO_4 in water at145 °C in an autoclave leads to the formation of high surface area $VOHPO_4{\cdot}0.5H_2O$. This confirms that if the reduction of V^{5+} to V^{4+} is achieved as the initial step then the hemihydrate can be formed in a water solvent in the autoclave method. Hence when HCl is used as the reducing agent it is clear that this must be carried out in the absence of phosphates if the reduction of V^{5+} to V^{4+} is to be achieved.

3.4. Comments on the potential reactivity and selectivity of the HP-VPA and HP-VPO materials

Based on the preceding discussion it is apparent that the HP-VPA method produces V^{5+} phosphates and principally $VOPO_4{\cdot}2H_2O$ with surface area of typically 1 m^2 g^{-1} whereas the HP-VPO method forms $VOHPO_4{\cdot}0.5H_2O$ with higher surface areas (HP-VPO-6 = 8 m^2 g^{-1}, HP-VPO-16 = 3 m^2 g^{-1}, and HP-VPO-72 = 2 m^2 g^{-1}). Activation and reactivity of $VOPO_4{\cdot}2H_2O$ and $VOHPO_4{\cdot}0.5H_2O$ precursors has been extensively studied previously [1–6,20,22] and consequently the potential reactivity and selectivity of the catalysts formed from the HP-VPA and HP-VPO catalyst precursors can be commented on. One striking feature of vanadium phosphate catalysts is that, in general,

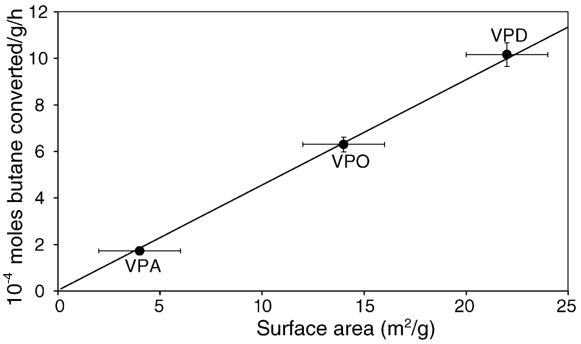

Fig. 10. Relationship between catalyst activity and surface area for standard vanadium phosphate catalysts for the oxidation of butane.

there is a linear relationship between catalyst activity and catalyst surface area [5,20,24]. This is shown in Fig. 10 for three standard vanadium phosphate catalysts prepared using ambient pressure methodology, namely VPA and VPO as described earlier in this paper, and a catalyst designated VPD prepared by alcohol reduction of $VOPO_4 \cdot 2H_2O$ [15,19–21,24]. The three catalysts all give very similar selectivities for maleic anhydride of ca. 55% [24] under the reaction conditions used (reaction conditions: 400 °C, 1.7% *n*-butane in air, GHSV = 2500 h^{-1}). Based on previous studies [33] activation of the HP-VPA catalysts is expected to lead to the formation of low area final catalysts (ca. 1 $m^2\ g^{-1}$) which would have an activity of $<1 \times 10^{-4}$ mol butane converted g catalyst $^{-1}$ h^{-1}. As the final catalysts derived from $VOPO_4 \cdot 2H_2O$ contain V^{5+} phosphates the selectivity to maleic anhydride would also be lower than the standard VPA catalysts. Consequently, the HP-VPA route is not expected to lead to high activity and high selectivity catalysts. In contrast the HP-VPO route led to higher area precursors and on activation, on the basis of previous studies [20], would yield catalysts comprising mainly $(VO)_2P_2O_7$ with surface areas between 2 and 10 $m^2\ g^{-1}$ which would give an activity of ca. (2–4) $\times 10^{-4}$ mol butane converted g catalyst $^{-1}$ h^{-1} under the standard reaction conditions (400 °C, 1.7% *n*-butane in air, GHSV = 2500 h^{-1}). The selectivity that can be expected for the HP-VPO catalysts is expected to be similar to that observed for the VPO catalysts prepared at ambient pressure.

Acknowledgements

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References

[1] G. Centi, Catal. Today 16 (1994) 1.
[2] E. Bordes, Catal. Today 1 (1987) 499.
[3] J.T. Gleaves, J.R. Ebner, T.C. Knechler, Catal. Rev. Sci. Eng. 30 (1988) 49.
[4] G. Centi, F. Trifirò, G. Busca, J. Ebner, J. Gleaves, Faraday Discuss. 87 (1989) 215.
[5] G.J. Hutchings, Appl. Catal. 72 (1991) 1.
[6] G. Centi, G. Fornasari, F. Trifirò, J. Catal. 89 (1984) 44.
[7] F. Cavani, G. Centi, F. Trifirò, J. Chem. Soc., Chem. Commun. (1985) 492.
[8] F. Trifirò, Catal. Today 16 (1993) 91.
[9] S. Albonetti, F. Cavani, F. Trifirò, P. Venturoli, G. Calestani, M.L. Granados, J.L.G. Fierro, J. Catal. 160 (1996) 52.
[10] F. Cavani, F. Trifirò, Appl. Catal. A: Gen. 157 (1997) 195.
[11] F. Trifirò, Catal. Today 41 (1998) 21.
[12] F. Cavani, F. Trifirò, Stud. Surf. Sci. Catal. 91 (1995) 1.
[13] G.J. Hutchings, A. Desmartin Chomel, R. Olier, J.C. Volta, Nature 368 (1994) 41.
[14] C.J. Kiely, A. Burrows, G.J. Hutchings, K.E. Bere, J.C. Volta, A. Tuel, M. Abon, J. Chem. Soc., Faraday Discuss. 105 (1996) 103.
[15] J.W. Johnson, D.C. Johnston, A.J. Jacobson, J.F. Brody, J. Am. Chem. Soc. 106 (1984) 8123.
[16] K. Ait-Lachgar, M. Abon, J.C. Volta, J. Catal. 171 (1991) 383.
[17] E.A. Lombardo, C.A. Sanchez, L.M. Conaglia, Catal. Today 15 (1992) 407.
[18] F. Ben Abdelouahab, J.C. Volta, R. Olier, J. Catal. 148 (1994) 334.
[19] I.J. Ellison, G.J. Hutchings, M.T. Sananes, J.C. Volta, J. Chem. Soc., Chem. Commun. (1994) 1093.
[20] C.J. Kiely, A. Burrows, S. Sajip, G.J. Hutchings, M.T. Sananes, A. Tuel, J.C. Volta, J. Catal. 162 (1996) 31.
[21] J. Haber, V.A. Zazhigalov, J. Storch, L.V. Bogutskaya, I.V. Bacherikova, Catal. Today 33 (1997) 39.
[22] G.J. Hutchings, M.T. Sananes, S. Sajip, C.J. Kiely, A. Burrows, I.J. Ellison, J.C. Volta, Catal. Today 33 (1997) 161.
[23] F.J. Cabello Sanchez, J.A. Lopez Sanchez, R.P.K. Wells, C. Rhodes, A. Isfahani, G.J. Hutchings, Catal. Lett. 77 (2001) 189.
[24] J.A. Lopez Sanchez, L. Griesel, J.K. Bartley, R.P.K. Wells, A. Liskowski, D. Su, R. Schlögl, J.C. Volta, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 3525.
[25] C. Qin, L. Xu, Y. Wei, X. Wang, F. Li, Inorg. Chem. 42 (2003) 3107.
[26] L.-I. Hung, S.-L. Wang, H.-M. Kao, K.-H. Lii, Inorg. Chem. 41 (2002) 3929.
[27] E. Le Fur, B. de Villoers, J. Tortelier, J.Y. Pivan, Inorg. Chem. 40 (2001) 272.
[28] A. Clearfield, J.M. Heising, B.G. Shpeizer, X. Ouyang, Int. J. Inorg. Mater. 3 (2001) 215.
[29] B.G. Shpeizer, X. Ouyang, J.M. Heising, A. Clearfield, Chem. Mater. 13 (2001) 2288.
[30] M.A. Carreon, V.V. Guliants, F. Pierelli, F. Cavani, Catal. Lett. 92 (2004) 11.
[31] M.A. Carreon, V.V. Guliants, M.O. Guerrero-Pérez, M.A. Banares, Micropor. Mesorpor. Mater. 71 (2004) 57.
[32] Y. Kamiya, S. Heki, N. Hiyoshi, N. Yamamoto, T. Okuhara, Catal. Lett. 78 (2003) 281.
[33] J.K. Bartley, C.J. Kiely, R.P.K. Wells, G.J. Hutchings, Catal. Lett. 72 (2001) 99.