Effect of group 13 compounds and bulky organic oxygenates as structural promoters for the selective oxidation of *n*-butane with vanadium phosphorus oxide catalysts

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A detailed study of *n*-butane oxidation over vanadium phosphate catalysts derived from *in situ* activation of $VOHPO_4 \cdot 0.5H_2O$ modified with group 13 compounds or 2-norbonanemethanol is described and discussed. Two methods of preparation of $VOHPO_4 \cdot 0.5H_2O$ were studied: (a) the VPO method, in which V_2O_5 is reacted with H_3PO_4 in isobutanol, and (b) the VPD method, in which $VOPO_4 \cdot 2H_2O$ is reacted with isobutanol. Group 13 additives (B, Al, Ga, In) were found to change the morphology of the VPO catalyst precursor from platelet-like to the rosette morphology usually associated with the VPD type of preparation. Although all act as structural modifiers, the In- and Ga-doped materials give improved catalyst performance for the synthesis of maleic anhydride from the selective oxidation of *n*-butane. The Al, Ga and In additives were added as acetylacetonates and it was found that addition of 1% acetylacetonate also enhances the catalyst performance, but does not act as a structural promoter. In view of this, the addition of 2-adamantanol and 2-norbonane methanol was investigated for the VPD-type preparation method. The addition of 2-norbonanemethanol was found to enhance the catalyst surface area of the activated catalyst, but the catalyst performance, with respect to both *n*-butane conversion and maleic anhydride selectivity, was not improved and this is considered to be due to the alcohol being strongly adsorbed on the catalyst surface.

Introduction

Vanadium phosphate compounds are used commercially as catalysts for the selective oxidation of *n*-butane for the production of maleic anhydride. At present, vanadium phosphates remain the only example of a heterogeneous catalyst employed commercially for the partial oxidation of an alkane. It is, therefore, not surprising that these catalysts have been extensively studied.[1–8] The current catalyst is prepared by *in situ* activation of $VOHPO_4 \cdot 0.5H_2O$ in a butane–air mixture under reaction conditions[5–7] which form a complex mixture of $(VO)_2P_2O_7$ and $VOPO_4$ phases.[6] Considerable progress has been made recently concerning the nature of active sites for the pure vanadium phosphate catalysts. *In situ* Raman spectroscopy suggests that specific combinations of V^{4+} and V^{5+} phases are a necessary requirement for the catalyst to exhibit high activity and high selectivity for the formation of maleic anhydride.[5] In addition, Coulston *et al.*[8] have shown that V^{5+} is essential for the initial activation of *n*-butane.

Although considerable progress has been achieved with pure vanadium phosphate, it should be noted that the catalysts used industrially contain a broad range of structural and electronic promoters. In particular, a wide range of cations have been added to vanadium phosphate catalysts and beneficial effects have been reported with: Co, Mo;[9] Co, Cd, Ni;[10] Zn, Bi, Cu, Li;[11–13] V;[14] Zr;[15] La[16] and Nb.[17] Most of this literature has been reviewed[4] and the promoters are considered to improve catalyst performance *via* two mechanisms. Firstly, the promoter can increase the surface area of the catalyst and, therefore, acts as a structural promoter. This is achieved by the metal cation acting as a phosphorus scavenger ensuring that inactive phases, such as the low surface area $VO(H_2PO_4)_2$ phase, are not formed.[18] Secondly, the metal cation can act as an electronic promoter by forming solid solutions of the type $[(VO)_{1-x}M_x]_2P_2O_7$,[19] where M represents a promoter cation, in which the promoter cation substitutes for V^{4+}. This may form defects in the structure which can act as new active sites or, alternatively, the metal cations may affect the redox properties of the surface. Recently, we have reported detailed studies on the structural and electronic effects of Co and Fe as catalyst promoters.[20,21] However, it is interesting to note that group 13 compounds have, to date, been neglected as additives, although it is known that Ga_2O_3 has been found to be very active for the activation of carbon–hydrogen bonds in alkanes.[22] In this paper, we investigate the effect of group 13 compounds as catalyst promoters. In particular, the interplay between structural and redox effects is examined in detail. In addition, the effect of using bulky alcohols as structural promoters is also explored.

Experimental

Catalyst preparation

Preparation of $VOHPO_4 \cdot 0.5H_2O$. $VOHPO_4 \cdot 0.5H_2O$ was prepared using the VPO and VPD preparation methods.[6,23] In the VPO method, V_2O_5 (11.8 g, Aldrich) was refluxed with H_3PO_4 (16.49 g, 85%, Aldrich) in isobutanol (250 ml, Aldrich) for 16 h. The light blue solid, $VOHPO_4 \cdot 0.5H_2O$, was recovered by vacuum filtration, washed with isobutanol (200 ml) and ethanol (250 ml) and refluxed with water (9 ml g^{-1}) for 3 h, filtered hot and dried in air (110 °C, 16 h). In the VPD method, V_2O_5 (11.8 g, Aldrich) was refluxed with H_3P_O4 (115 g, 85%, Aldrich) in water (300 ml) for 8 h. The yellow solid,

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$VOPO_4 \cdot 2H_2O$, was recovered by vacuum filtration, washed with cold water and acetone and dried in air (110 °C, 16 h). The resulting dried $VOPO_4 \cdot 2H_2O$ (2 g) was refluxed in isobutanol (40 ml) for 21 h. The blue solid, $VOHPO_4 \cdot 0.5H_2O$, was recovered by vacuum filtration, washed with isobutanol (200 ml) and ethanol (250 ml), refluxed in water (10 ml g^{-1}) for 2 h, filtered hot and dried (110 °C, 16 h).

Preparation of $VOHPO_4 \cdot 0.5H_2O$ containing group 13 compounds. The VPO method, described above, was used and the appropriate group 13 compounds were added, together with the V_2O_5 at the start of the preparation. The following compounds were used: aluminium acetylacetonate (0.41 g, Aldrich), gallium acetylacetonate (0.51 g, Aldrich), indium acetylacetonate (0.54 g, Aldrich), tributylborate (0.31 g, Aldrich), acetylacetone (0.129 g, Aldrich), tributylaluminate (0.31 g, Aldrich). The materials were analysed using ICPMS and the promoter/V molar ratios for the acetylacetonate compounds were found to be $Al/V = 0.014$, $Ga/V = 0.014$, $In/V = 0.012$ and, for the tributyl compounds $Al/V = 0.01$ and $B/V = 0.009$.

Preparation of $VOHPO_4 \cdot 0.5H_2O$ with mixed alcohols. The VPD method, described above, was used and the appropriate bulky alcohol (2-norbonanemethanol, 2-adamantanol) was added with the isobutanol at the stage when $VOPO_4 \cdot 2H_2O$ was refluxed in the alcohol.

Catalyst testing and characterisation

The oxidation of *n*-butane was carried out using a microreactor and a standard volume of catalyst (0.7 ml). *n*-Butane and air were fed into the reactor *via* calibrated mass flow controllers to give a feedstock composition of 1.8% *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. $VOHPO_4 \cdot 0.5H_2O$ precursors were activated *in situ* (1.8% *n*-butane in air, 2500 h^{-1}) at 400 °C for 72 h.

A number of physical techniques were employed to characterise the catalyst microstructure. Powder X-ray diffraction (PXRD) was performed using an Enraf Nonius FR590 X-ray generator with a Cu-Kα source fitted with an Inel CPS 120 hemispherical detector. BET (Brunauer–Emmett–Teller) 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 using a Hitachi S-2460 N SEM, operating at an accelerating voltage of 25 kV. Inductively coupled plasma mass spectroscopy (ICPMS) was performed using a Perkin Elmer Elan 5000 ICP mass spectrometer.

Results and discussion

Vanadium phosphate catalysts modified with group 13 compounds

Catalyst precursor characterisation. Catalyst precursors containing *ca.* 1 mol% group 13 compounds were prepared using the modified VPO method and the laser Raman spectra and PXRD patterns are shown in Fig. 1 and 2, respectively. The laser Raman spectra (Fig. 1) do not show much detail due to the fluorescence caused by the retention of the alcohol within the catalyst precursor crystallites. However, the main band at a Raman shift of 984 cm^{-1} with minor bands at Raman shifts of 1151, 1110 and 340 cm^{-1} can all be assigned to $VOHPO4 \cdot 0.5H_2O$[24,25] (1151 and 1110 cm^{-1}, V–O–P; 984 cm^{-1}, P–O stretch; 340 cm^{-1}, coupled V–O and P–O bonding mode). All the reflections in the PXRD patterns (Fig. 2) can be indexed to $VOHPO_4 \cdot 0.5H_2O$.[26] No reflections are observed that can be indexed to separate phases of group 13 compounds. The PXRD patterns show an interesting difference when the group 13 additive is present (Fig. 2) compared to the unpromoted VPO material. For the unpromoted $VOHPO_4 \cdot 0.5H_2O$, the main reflection corresponds to the *d*-spacing of 0.57 nm and can be indexed to the (001) plane. However, addition of group 13 additives, in all cases leads to the reflections at $d = 0.29$ nm, indexed to the (220) plane, being the most intense reflection in the pattern, as is typically observed with the VPD method of preparation.[23] To determine if the organic ligands, *i.e.* the butoxy or acetylacetonate, could cause this restructuring, a separate experiment was carried out in which 1% acetylacetone was added to the VPO

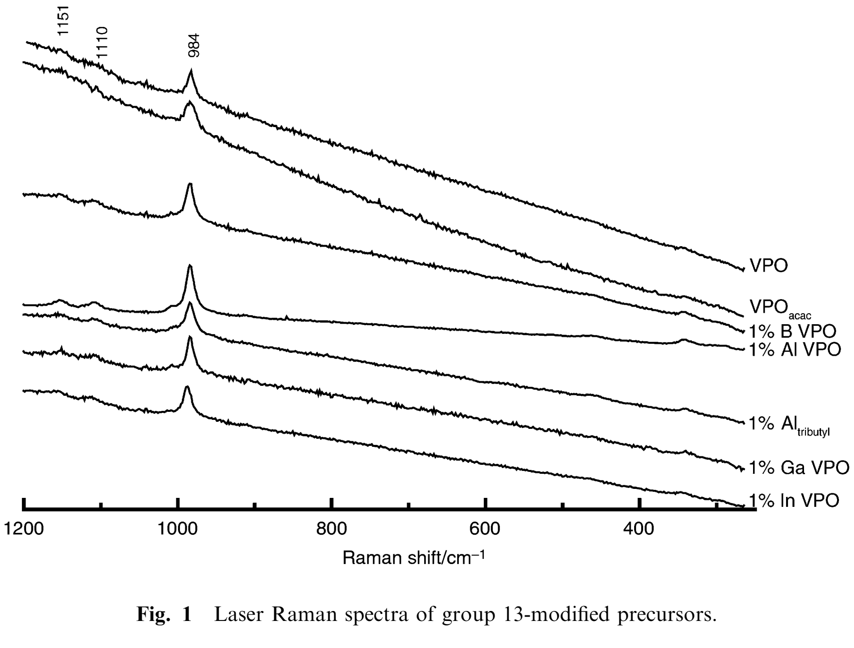


Fig. 1 Laser Raman spectra of group 13-modified precursors.

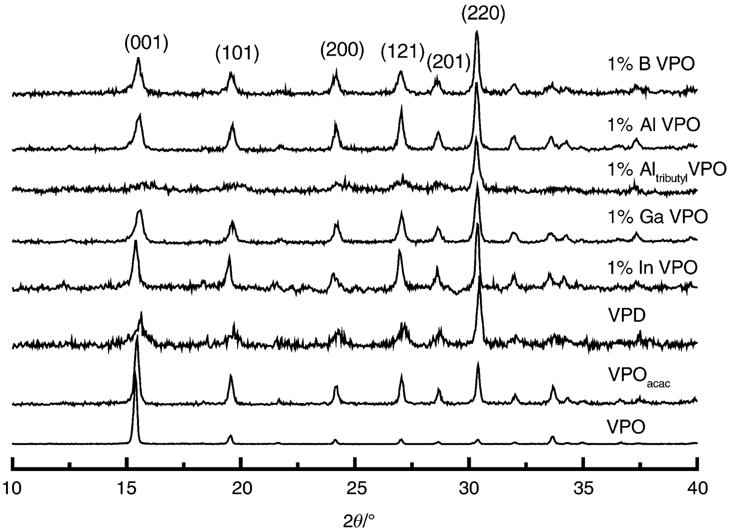


Fig. 2 Powder XRD patterns of group 13-modified precursors.

preparation method. The PXRD pattern, shown in Fig. 2, is identical to that for $VOHPO_4 \cdot 0.5H_2O$ prepared analogously in the absence of acetylacetone. Hence, it can be concluded that the changes observed in the PXRD pattern can be ascribed to the presence of the group 13 element. A similar PXRD pattern was observed for the aluminium-doped material prepared using either aluminium acetylacetonate or tributylaluminate, which is a further indication that it is the group 13 element that is responsible for the differences observed. It is interesting to note that the PXRD pattern of the group 13-doped precursors is very similar to that of $VOHPO_4 \cdot 0.5H_2O$ prepared using the VPD method (Fig. 2). SEM micrographs for these precursors are shown in Fig. 3. The materials containing group 13 additives all display thin platelets of $VOHPO_4 \cdot 0.5H_2O$ and often these are associated with each other in the form of small spheres, similar to the rosette morphology of undoped $VOHPO_4 \cdot 0.5H_2O$ prepared by the VPD method. This is particularly marked for the aluminium-doped material. The SEM of the VPD-prepared material is shown for comparison and the morphology observed is consistent with the PXRD patterns in which the main reflection can be indexed to the (220) plane.[26] In contrast, the SEM micrographs for $VOHPO_4 \cdot 0.5H_2O$ prepared using the VPO method, in the presence or absence of 1% acetylacetone, have a more plate-like morphology [Fig. 3(e) and (f)] which is in agreement with the PXRD pattern, for which the main reflection can be indexed to the (001) phane.[26] Surface area measurements (Table 1) show that the addition of 1% acetylacetone does not affect the precursor surface area, but the addition of the group 13 additives does increase the surface area in all cases. The surface area of the B-doped material is markedly higher than the other additives, but this was prepared using tributylborate as the boron source as boron acetylacetonate is unavailable. The Al-doped material similarly prepared using tributylaluminate also has a higher surface area (12 m^2 g^{-1}), in contrast to 9 m^2 g^{-1} for the Al-doped material prepared using aluminium acetylacetonate. This indicates that the surface area of the precursor can be sensitive to the nature of the organic ligand added with the promoter.

***n*-Butane oxidation and post-reaction characterisation.** The group 13-doped $VOHPO_4 \cdot 0.5H_2O$ precursors were used as catalyst precursors for the oxidation of *n*-butane. The catalysts were activated *in situ* in the reactor with flowing *n*-butane (1.8%) in air at 400 °C for 72 h. During this time, the conversion of *n*-butane gradually increased [Fig. 4(a)] and the selectivity to maleic anhydride also increased [Fig. 4(b)]. The results are summarised in Table 1. The surface area of the activated catalysts was found to increase markedly for all the catalysts tested, with the highest surface area being observed with the B-doped material (31 m^2 g^{-1}). All the catalysts exhibited intrinsic activities (mol maleic anhydride m^{-2} h^{-1}) and specific activities (mol maleic anhydride g^{-1} h^{-1}) in similar ranges to that of the undoped catalysts. However, the specific activity of the In-doped material and the intrinsic activity of the Ga-doped material are both higher than the undoped catalyst or the catalyst prepared with 1% acetylacetone as additive. The slight promotional effect observed with In with respect to activity, and also the small promotional effect on selectivity observed with B, are much less marked than the effects observed previously with Co and Mo additives.[4]

The PXRD patterns for the activated catalysts are shown in Fig. 5 and the materials all have similar patterns that can be indexed to poorly crystalline $(VO)_2P_2O_7$.[26] There does not appear to be any marked difference between the XRD patterns of the undoped and doped activated catalysts. The laser Raman spectra of the activated catalysts do, however, show very clear differences (Fig. 6). The B-, Al-, Ga- and In-doped activated catalysts all show the two main Raman shifts at 926 and 1189 cm^{-1} that can be assigned to $(VO)_2P_2O_7$.[24,25] The two undoped activated catalysts all show additional bands, and these can be assigned to V^{5+} phases being present.[24,25] It should be noted that the broad band observed at 933 cm^{-1} for the undoped material is considered to be a combination of two bands at 927 and 939 cm^{-1}, which are resolved in the Raman spectrum for the activated undoped catalyst containing 1% acetylacetonate. The bands at 1089, 994, 939 and 470 cm^{-1} can be assigned to α_{II}-$VOPO_4$[25] and the bands at 1089, 1072, 1016 and 939 cm^{-1} can be assigned to γ-$VOPO_4$.[25] Thus, the presence of the group 13 additive, in combination with the organic ligand, appears to increase the level of reduction of the catalyst surface. However, this does not appear to affect the intrinsic activity of the catalyst significantly. Such a finding has been previously noted for catalysts prepared using the VPO and VPD methodologies[26] since, although the catalyst comprised different amounts of the $(VO)_2P_2O_7$ and $VOPO_4$ phases, they exhibited the same intrinsic activity. This has been assigned[27] to the activated catalysts having the same surface composition, which is considered to be amorphous in nature.

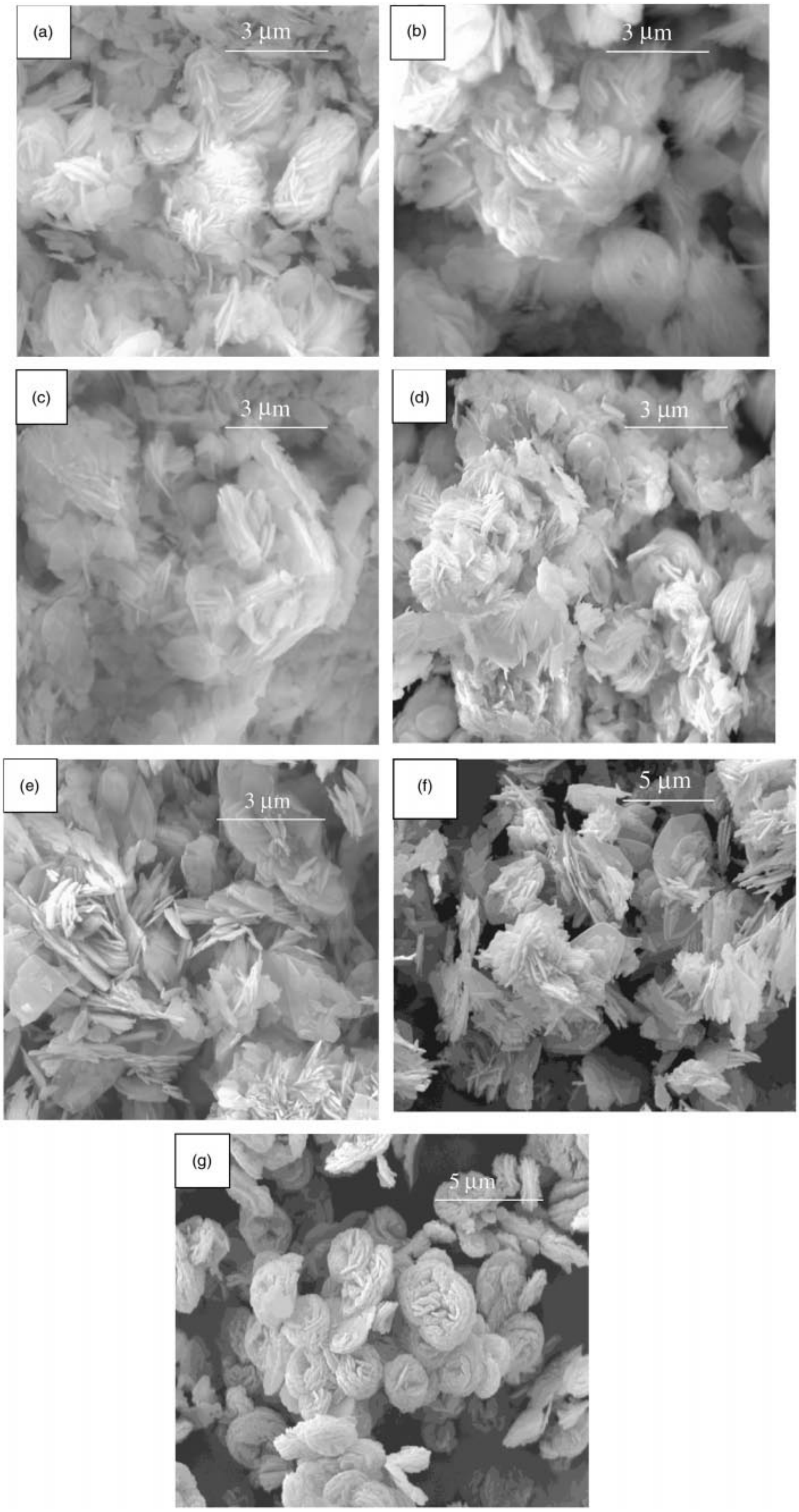


Fig. 3 SEM micrographs of modified precursors: (a) Al-doped, prepared using aluminium acetylacetonate; (b) Ga-doped; (c) In-doped; (d) B-doped; (e) 1% acetylacetonate added to preparation; (f) standard unpromoted VPO method with isobutanol; (g) standard unpromoted VPD method with isobutanol.

Table 1 *n*-Butane oxidation over catalysts derived from group 13-doped vanadium phosphates[a]

	Surface Area/$m^2\ g^{-1}$			Selectivity (%)				
Catalyst additive	Precursor	Activated catalyst	*n*-Butane conversion (%)	MA[b]	CO	CO_2	Intrinsic activity/ 10^{-5} mol MA[b] $m^{-2}\ h^{-1}$	Specific activity/ 10^{-4} mol MA[b] $g^{-1}\ h^{-1}$
None	7	25	64	56	17	27	1.79	4.48
1% acetylacetone	7	21	55	59	16	22	1.96	4.18
B[a]	14	31	55	62	14	22	1.42	4.40
Al[d]	9	21	58	52	15	33	1.85	3.89
Ga[d]	10	16	54	53	16	31	2.22	3.55
In[d]	9	25	67	57	17	22	1.90	4.85

[a] 1.8% *n*-butane in air, 400 °C, 2500 h^{-1}, 72 h. [b] MA = maleic anhydride. [c] Tributylborate. [d] Acetylacetonate.

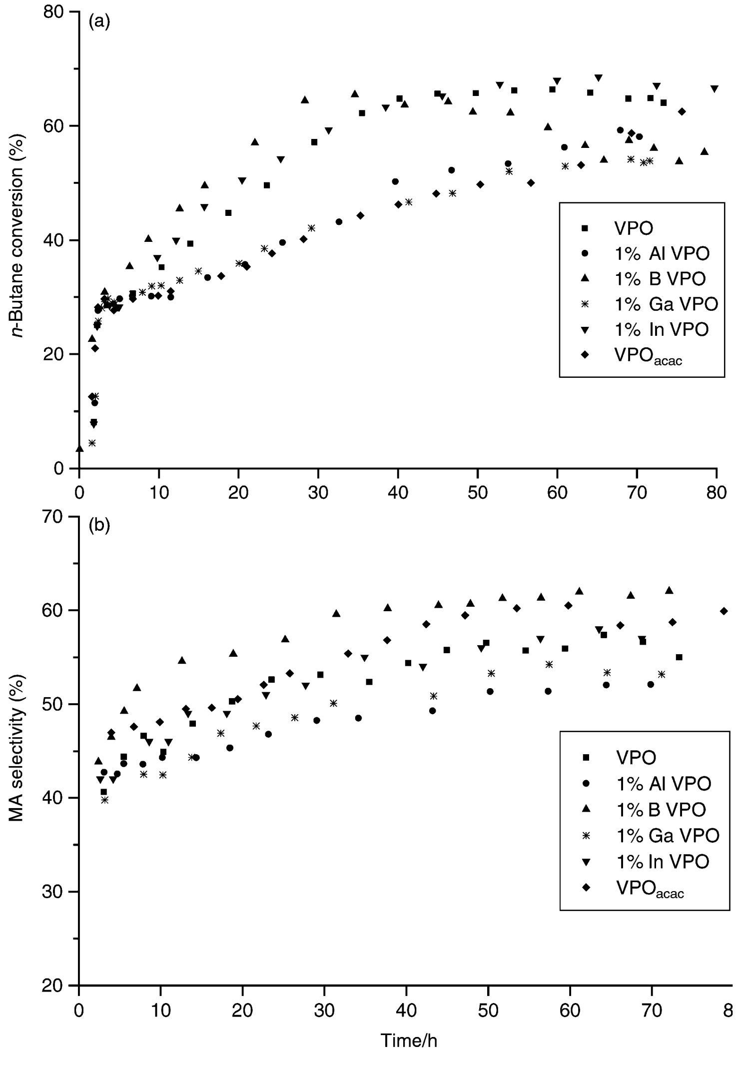


Fig. 4 Oxidation of *n*-butane to maleic anhydride showing the effect of catalyst activation (400 °C, 18% *n*-butane, 2500 h^{-1}) on (a) *n*-butane conversion and (b) maleic anhydride selectivity.

With respect to the intrinsic activity of the group 13-doped activated catalysts, it is apparent that, with the exception of the Ga-doped catalyst, the activities are very similar for the undoped and Al- and In-doped materials. This indicates that these additives are acting primarily as structural promoters rather than as electronic promoters. This is consistent with effects observed in the PXRD patterns and SEM images for the precursor materials. The inclusion of a group 13 element, in combination with the organic ligand, in the VPO method of preparation appears to result in a material that would normally be expected for the VPD methodology.[26] However, it is notable that: (i) the inclusion of 1% acetylacetone in the preparation leads to an increase in the intrinsic activity of the doped material by *ca.* 10% and (ii) the use of a tributylaluminate rather than aluminium acetylacetonate increases the surface area of the $VOHPO_4 \cdot 0.5H_2O$ precursor from 9 to 12 $m^2\ g^{-1}$. Both of these effects indicate that structural effects may be expected to arise from the addition of bulkier oxygenates to the preparation method and this is explored in the next section.

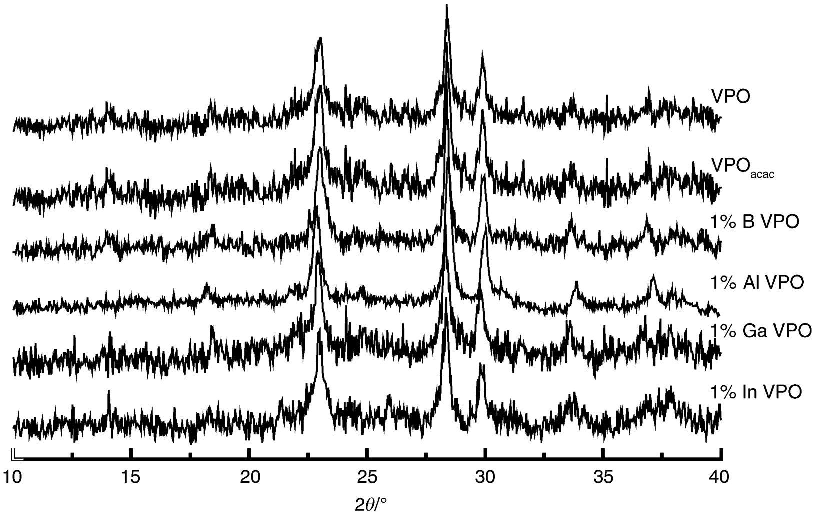


Fig. 5 Powder XRD patterns of group 13-modified activated catalysts.

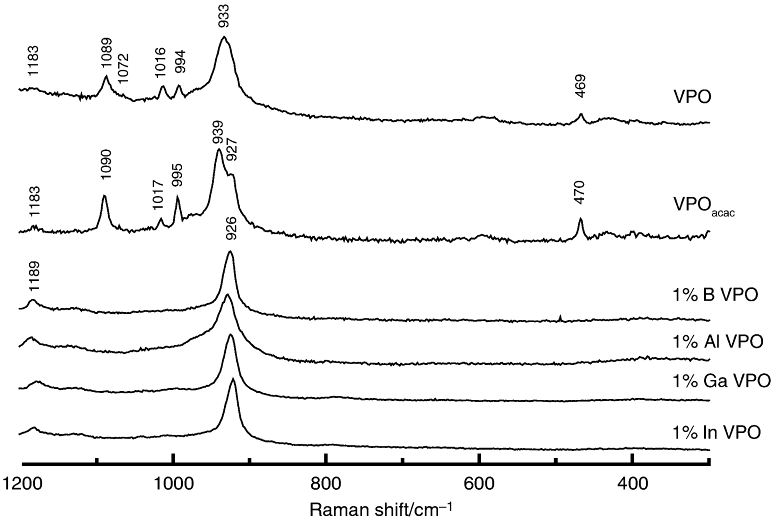
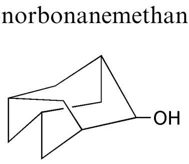


Fig. 6 Laser Raman spectra of group 13-modified activated catalysts.

Vanadium phosphate catalysts modified with 2-adamantanol and 2-norbonanemethanol

Catalyst precursor characterisation. Previous studies using 1-octanol in place of isobutanol in the VPD method of preparation of $VOHPO_4 \cdot 0.5H_2O$ have shown that the longer chain alcohol consistently gave higher surface area catalyst precursors and activated catalysts.[23] This effect is probably caused by the alcohol being occluded within the layer structure of the hemihydrate. Catalyst precursors were prepared using the VPD method in which 2-adamantanol (**1**) and 2-norbonanemethanol (**2**) were added to the isobutanol.



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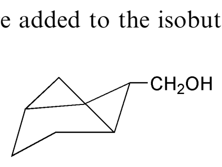

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2-Adamantanol. A series of catalyst precursors were prepared using the VPD method in which 2-adamantanol was added to the isobutanol during the alcohol reduction step of the preparation. Three different concentrations of 2-adamantanol were studied (0.01, 0.06 and 0.2 mol 2-adamantanol per mol isobutanol) and the PXRD patterns are shown in Fig. 7. All the reflections can be indexed to $VOHPO_4 \cdot 0.5H_2O$, although, in the preparation with the highest concentration of 2-adamantanol, it is clear that some crystalline 2-adamantanol is present. The laser Raman spectra showed the standard bands that can be assigned to $VOHPO_4 \cdot 0.5H_2O$.[24,25] The addition of 2-adamantanol did not markedly affect the surface area of the precursor (Table 2), although the addition of a small amount appears to decrease the surface area. In the powder X-ray diffraction pattern, it is notable that the precursors prepared using 2-adamantanol all give a pattern for which the $d = 0.57$ nm reflection is the most intense, and this is assigned to the (001) plane of $VOHPO_4 \cdot 0.5H_2O$. These PXRD patterns differ from that of the standard material prepared by the VPD method in the absence of 2-adamantanol, for which the reflection at $d = 0.29$ nm is the most intense. The PXRD patterns for the precursors prepared using 2-adamantanol are similar to those for the standard VPO catalyst (Fig. 2) and also to those prepared using the VPD method with alcohols other than primary alcohols as reducing agents.[23,26] This indicates that the 2-adamantanol is acting as the reducing agent in these reactions and, consequently, this affects the morphology of the $VOHPO_4 \cdot 0.5H_2O$. In view of this, further studies were conducted using a bulky primary alcohol, 2-norbonanemethanol.

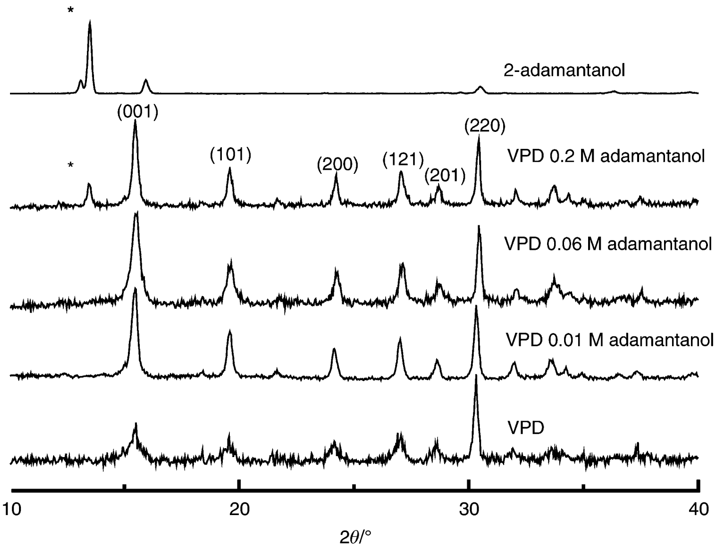

Fig. 7 Powder XRD patterns of 2-adamantanol precursors.

Table 2 Surface area of catalyst precursors

Catalyst precursor	Surface area/m^2 g^{-1}
Undoped VPD	18
0.01[b]	14
0.06[b]	20
0.20[b]	18
3[c]	14
10[c]	12
16[c]	27
33[c]	20
50[c]	9

[a] Standard preparation procedure. [b] Mol 2-adamantanol/mol isobutanol. [c] % 2-norbonanemethanol.

2-Norbonanemethanol. A series of catalysts were prepared using the VPD method in which 2-norbonanemethanol was added to the isobutanol. Five different concentrations of 2-norbonanemethanol were studied (3, 10, 16, 33 and 50 vol% 2-norbonanemethanol in isobutanol) and the PXRD patterns are shown in Fig. 8. All the reflections can be indexed to $VOHPO_4 \cdot 0.5H_2O$ and the most intense reflection is for $d = 0.29$ nm [assigned to the (220) plane], which is consistent with the PXRD pattern of $VOHPO_4 \cdot 0.5H_2O$ prepared in the absence of 2-norbonanemethanol (Fig. 8). This is to be expected, since both alcohols are primary alcohols.[23] The laser Raman spectra of the precursors prepared with 2-norbonanemethanol show no differences to the standard undoped catalyst precursor and all the bands can be assigned to $VOHPO_4 \cdot 0.5H_2O$. The most significant effect observed when 2-norbonanemethanol is included in the preparation concerns the surface area of the precursor (Table 2). The addition of a small amount of 2-norbonanemethanol (3, 10 vol%) leads to a marked decrease in the surface area, but higher concentrations up to 33 vol% lead to an increase in surface area. This indicates that the two alcohols used have a complex effect on the porosity of the catalyst precursor.

n-Butane oxidation and post-reaction characterisation of catalysts prepared using 2-norbonanemethanol. Representative $VOHPO_4 \cdot 0.5H_2O$ precursors prepared with the addition of 2-norbonanemethanol (0 vol%, standard VPD catalyst; 10 vol%, reduction in precursor surface area; 16 vol%, increase in precursor surface area) were used as catalyst precursors for the oxidation of *n*-butane. The catalysts were activated *in situ* in flowing *n*-butane (1.8%) in air at 400 °C for 12 h. During this time, the *n*-butane conversion and maleic anhydride selectivity increased and stabilised. The results

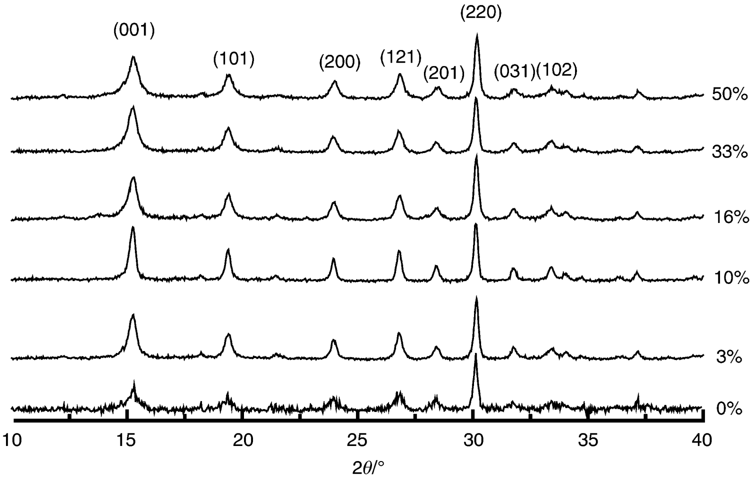

Fig. 8 Powder XRD patterns of 2-norbonanemethanol precursors.

from the activated catalysts are given in Table 3. The surface areas of the activated catalysts were found to be significantly higher than those of the precursors, and the two catalysts prepared using 2-norbonanemethanol gave much higher surface areas than the standard catalyst. The PXRD patterns and the laser Raman spectra of the activated catalysts are shown in Fig. 9 and 10 respectively. All reflections in the PXRD patterns can be assigned to $(VO)_2P_2O_7$ and all the bands in the Raman spectra can similarly be assigned to $(VO)_2P_2O_7$.[24,25] It is apparent that these characterisation methods do not show any major differences in the activated catalysts, which can be classified as poorly crystalline $(VO)_2P_2O_7$. However, the catalytic performance of the 2-norbonanemethanol catalysts is, unfortunately, poorer than the standard catalyst. In particular, both the *n*-butane conversion and selectivity to maleic anhydride decrease with

Table 3 *n*-Butane oxidation over catalysts derived from group 13-doped vanadium phosphates

	Surface Area/$m^2\ g^{-1}$			Selectivity (%)				
Catalyst/ % 2NBM[a]	Precursor	Activated catalyst	n-Butane conversion (%)	MA[b]	CO	CO_2	Intrinsic activity/ 10^{-5} mol MA[b] $m^{-2}\ h^{-1}$	Specific activity/ 10^{-4} mol MA[b] $g^{-1}\ h^{-1}$
0	18	22	65	58	23	19	2.39	5.26
10	12	27	60	56	27	17	1.70	4.59
16	27	35	45	55	22	23	1.01	3.54

[a] 1.8% *n*-butane in air, 400 °C, 2500 h^{-1}, 72 h, 2NBM = 2-norbonanemethanol. [b] MA = maleic anhydride.

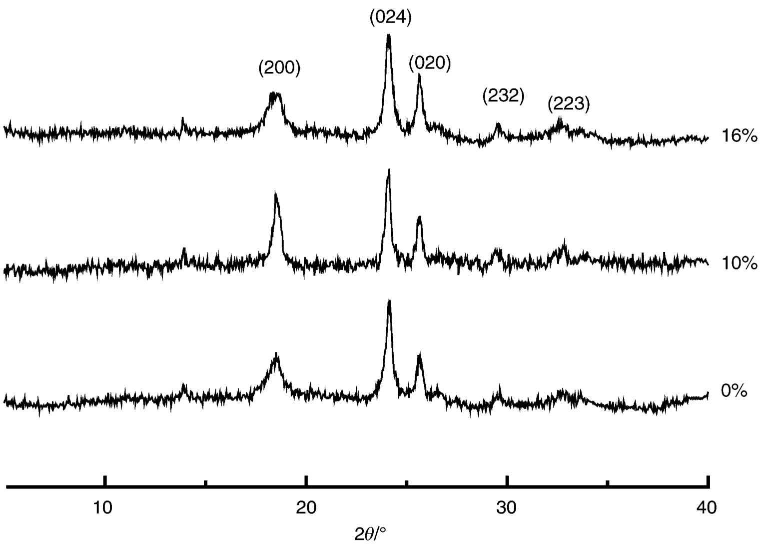

Fig. 9 Powder XRD patterns of 2-norbonanemethanol-activated catalysts.

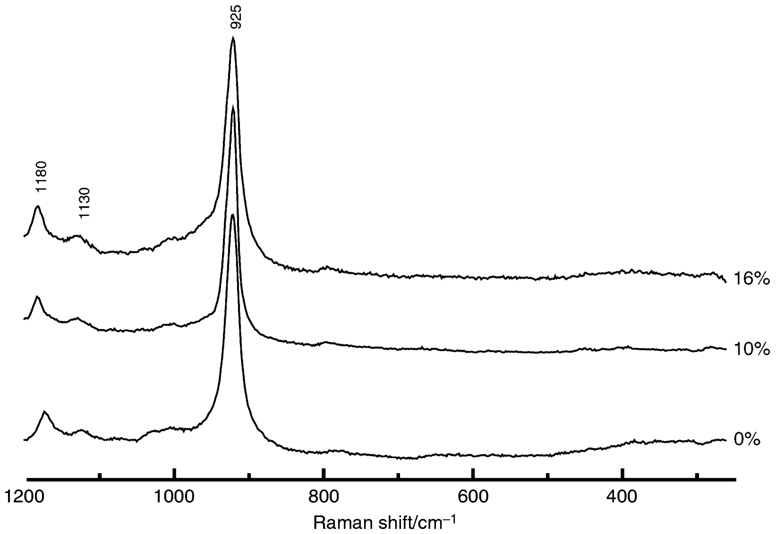

Fig. 10 Laser Raman spectra of 2-norbonanemethanol-activated catalysts.

increasing 2-norbonanemethanol concentration, even though the surface area of the catalysts increases. Consequently, both the specific activity (mol maleic anhydride g^{-1} h^{-1}) and intrinsic activity (mol maleic anhydride m^{-2} h^{-1}) decrease when 2-norbonanemethanol is added to isobutanol.

The results of this study confirm that the use of bulky reducing agents, as previously demonstrated with 1-octanol,[23] can significantly enhance the surface area of activated vanadium phosphate catalysts. However, although they can, in principle, act as structural promoters, it is apparent that very bulky alcohols do not enhance catalyst performance. This may be due to the bulky alcohol being strongly adsorbed on the catalyst surface from where it is not readily desorbed during the activation process.

Conclusions

Group 13 additives (B, Al, Ga, In) are found to change the morphology of the VPO catalyst precursor (prepared by the reaction of V_2O_5 with H_3PO_4 in isobutanol) from plate-like to rosette morphology. The rosette morphology is normally associated with the VPD catalyst precursor (prepared by the reaction of $VOPO_4 \cdot 2H_2O$ with isobutanol). Although, all the additives act as structural modifiers, the In- and Ga-doped materials also enhance the catalyst performance for the selective oxidation of *n*-butane.

The addition of 2-norbonanemethanol in the VPD precursor preparation was found to affect the surface area of the material, but the catalyst performance was not enhanced. This is considered to be due to the alcohol being strongly adsorbed on the catalyst surface.

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