

Promotion of vanadium phosphate catalysts using gallium compounds: effect of low Ga/V molar ratios

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Abstract

The doping of vanadium phosphate catalysts by low levels of gallium is described and discussed. $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursors doped with Ga were prepared using a two stage method in which V_2O_5 is initially reacted with isobutanol before reaction with H_3PO_4 and $\text{Ga}(\text{acac})_3$. 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 for 72 h. The materials were characterised using a combination of powder XRD, BET surface area measurement, laser Raman spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy. The addition of 0.1 mol% Ga significantly enhances the activity of the catalyst. The effect is due in part to a structural effect as the surface area of the catalyst is increased by ca. 50–100% when up to 1 mol% Ga is added. However, the intrinsic activity (mol maleic anhydride produced/m²/h) is also significantly enhanced at these low doping levels. Hence, the promotional effect is considered to be due to both structural and electronic effects. The source of Ga was found to be and experiments were carried out with Ga_2O_3 and GaPO_4 in place of $\text{Ga}(\text{acac})_3$. GaPO_4 was found to give some enhancement in activity, but neither Ga_2O_3 nor GaPO_4 gave an enhancement in surface area.

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1. Introduction

Vanadium phosphate catalysts represent one of the most well studied heterogeneous catalysts since they remain one of the few known catalysts capable of selective oxidation of alkanes [1–5]. One of the key areas of study, mainly described in the patent literature [5], is the promotion of these catalysts by low levels of metal compounds. In an earlier comprehensive review of the literature on this topic [5], promoters were considered to act in two ways; namely, structural effects due to an enhancement in the surface area of the activated catalysts and electronic which has been demonstrated in very few systems to date. The addition of low levels of Mo [5,6] is found to enhance both selectivity and

activity whereas the addition of low levels of Co affects mainly the activity [7–10]. The structural effects usually occur by the promoter cation acting as a phosphorus scavenger, thereby, ensuring that inactive low surface area phases such as $\text{VO}(\text{H}_2\text{PO}_4)_2$ are not formed [5,11]. The excess phosphorus is typically present in these promoted catalysts as the phosphate of the added cation [11]. The metal cation may occasionally also act as an electronic promoter by forming solid solutions of the type $[(\text{VO})_{1-x}\text{M}_x]_2\text{P}_2\text{O}_7$ [12,13] where M represents a promoter cation that substitutes for V^{4+} . In this way, the $\text{V}^{4+}/\text{V}^{5+}$ ratio can be significantly affected and this can enhance activity [14]. Alternatively, the substitution of V^{4+} by a M^{2+} or M^{3+} cation can introduce defects into the catalyst and these can act as new active centres.

In this paper, we explore the promotion of vanadium phosphate catalysts by gallium doping. Until recently, there has been very little interest shown in doping by group 13 cations. This is somewhat surprising since Ga has been shown to be

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effective as a catalyst component in the activation of methane and the $\text{CH}_4\text{-D}_2$ exchange reaction [15]. Recently, we have shown that Ga can act as a promoter for vanadium phosphate catalysts [16] and in a related study we have made a detailed study of the structure of Ga-doped vanadium phosphate catalysts doped with Ga and have found that Ga acts as both a structural and an electronic promoter [17]. In this paper, we extend these earlier studies and examine the effects of low levels of Ga doping and observe a pronounced promotion in catalyst performance for catalysts doped with 0.1 mol% Ga, which is significantly lower than the levels of Ga-dopant in our previous studies [16,17].

2. Experimental

2.1. Catalyst preparation

An undoped $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor was prepared by refluxing V_2O_5 (11.8 g, Strem) in isobutanol (250 ml) for 18 h. H_3PO_4 (16.49 g, 85%, Aldrich) was then added and the mixture was refluxed for a further 18 h. The light blue solid was recovered by filtration, washed with isobutanol (200 ml) and ethanol (150 ml, 100%) and dried. The solid was refluxed in water (9 ml/g solid), filtered hot and dried in air (110 °C, 16 h). The doped precursors were prepared using the same procedure except $\text{Ga}(\text{acac})_3$ was added with the V_2O_5 in the initial reflux step and the catalysts precursors were not refluxed with water. The amounts of $\text{Ga}(\text{acac})_3$ added are as follows for the catalysts: 0.0235 g (0.1 mol%), 0.117 g (0.5 mol%), 0.235 g (1.0 mol%), 0.352 g (1.5 mol%). A blank material was prepared in an analogous manner in which acetylacetone (1 mol%, Aldrich) was added with the V_2O_5 in the initial reflux step. To investigate the role of the gallium compound, two additional catalyst samples were prepared using Ga_2O_3 (1% based on V, 0.06 g, Aldrich) or GaPO_4 (1% based on V, 0.1054 g) which was also added with the V_2O_5 in the initial reflux step.

A sample of GaPO_4 was prepared using a novel method as follows. $\text{Ga}(\text{acac})_3$ (3.0 g, Aldrich, 98%) was refluxed in isobutanol (125 ml, Aldrich) for 18 h. H_3PO_4 (0.95 g, 85%, Aldrich) was then added and the mixture was refluxed for a further 16 h. The material was recovered by filtration, washed with isobutanol (200 ml) and ethanol (100 ml, 100%), dried and calcined at 500 °C for 2 h.

2.2. Catalyst testing and characterisation

The oxidation of *n*-butane was carried out in a microreactor with a standard mass of catalyst (0.25 g). *n*-Butane and air were fed to the differential Pyrex reactor (U-tube) via calibrated mass flow controllers to give a feedstock composition of 1.6% *n*-butane, 18% O_2 and 80.4% He with a GHSV of 2000 h^{-1} . The products were then fed via heated lines to an on-line gas chromatograph for analysis. The reactor comprised a Pyrex glass reactor 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 (1.6% *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 both the precursor and activated the catalyst structure. Powder X-ray diffraction (XRD) was performed using an Enraf Nonius FRS 590 X-ray generator with a Cu $\text{K}\alpha$ source fitted with an Inel CPS 120 hemispherical detector. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics ASAP 2000 instrument. Raman spectra were obtained using a Renishaw Ramanscope Spectrograph fitted with a green Ar^+ laser ($\lambda = 514.532\text{ nm}$). Scanning electron microscopy (SEM) was performed on a Hitachi 326YO-N instrument operating at 20 kV. Atomic emission spectroscopy (AES-ICP) was used to determine the atomic composition of the vanadium phosphate catalysts using a D Spectroflamme ICP.

3. Results and discussion

3.1. Catalyst precursor preparation and characterisation

A series of vanadium phosphate precursors was prepared using the two stage method containing nominally 0, 0.1, 0.5, 1.0 and 1.5 mol% Ga based on V. In addition, two samples containing 1 mol% Ga prepared using Ga_2O_3 and GaPO_4 were also prepared. To determine the effect of the organic fragment of the additive a catalyst made with 1 mol% acetylacetone was also prepared. The Ga analysis as well as the surface areas of the precursors are given in Table 1. The addition of these low levels of Ga using $\text{Ga}(\text{acac})_3$ increased the surface area significantly but this was not observed with the other Ga compounds. However, it is apparent that the sample prepared using 1 mol% acetylacetone gives the same enhancement in surface area, and consequently, we conclude that the increase in surface area is related to the acac ligand and not specifically the Ga.

The powder X-ray diffraction patterns of the precursors are shown in Figs. 1–4. In all cases the reflections can be indexed to the hemihydrate precursor $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and no reflections of Ga compounds are apparent. The addition of 0.1 mol% Ga does not significantly affect the powder X-ray diffraction pattern. However, the addition of higher concentrations leads to a significant decrease in the intensity of the [00 1] reflection relative to the [2 2 0] reflection. This is particularly marked for the 1 mol% Ga sample prepared from $\text{Ga}(\text{acac})_3$. However, this is not observed for the samples prepared with the other Ga compounds. Furthermore, it is not observed with the material prepared using 1 mol% acetylacetone. Consequently, this effect appears to be due specifically to the use of $\text{Ga}(\text{acac})_3$ as the gallium source. The Raman spectra all were consistent with the spectrum of

Table 1
Catalyst performance of vanadium phosphate for the oxidation of *n*-butane

Precursor	Ga/V (mol ratio)	Surface area (m ² /g)		<i>n</i> -Butane conversion (%)	Maleic anhydride selectivity (%)	Intrinsic activity (10 ⁻⁵ mol MA/m ² /h)
		P ^a	C ^a			
VPO	–	8	15	22	55	2.92
VPO–0.1% Ga ex Ga(acac) ₃	0.105	16	26	73	51	4.27
VPO–0.5% Ga ex Ga(acac) ₃	0.52	13	22	72	62	4.47
VPO–1.0% Ga ex Ga(acac) ₃	1.07	25	30	56	56	3.71
VPO–1.5% Ga ex Ga(acac) ₃	1.51	19	20	40	53	3.05
VPO–1.0% Ga ex Ga ₂ O ₃	0.7	10	11	24	45	3.04
VPO–1.0% Ga ex GaPO ₄	0.97	11	12	30	55	3.33
VPO–1.0% acac	–	16	14	21	37	2.13
GaPO ₄	–	52	50	3	4	0.007

^a P denotes precursor and C denotes activated catalyst.

the hemihydrate but all were relatively indistinct due to fluorescence resulting from the occlusion of isobutanol within the precursor structure. The morphology of the precursors was examined using scanning electron microscopy (Fig. 5) and all showed very similar platelet morphology typical of

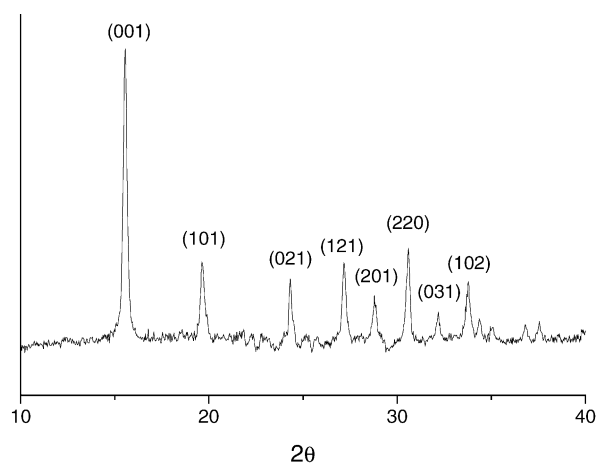


Fig. 1. Powder X-ray diffraction pattern of the undoped precursor.

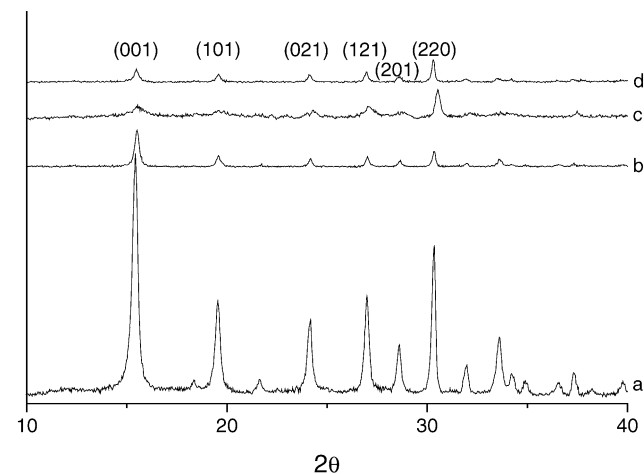


Fig. 2. Powder X-ray diffraction pattern of the doped precursors derived from Ga(acac)₃: (a) 0.1% Ga; (b) 0.5% Ga; (c) 1.0% Ga and (d) 1.5% Ga.

the undoped precursor. The micrographs shown are fully representative of the morphology of the samples. Increasing the amount of Ga(acac)₃ decreased the size of the platelets for the 0.5 and 1 mol% samples but at higher concentra-

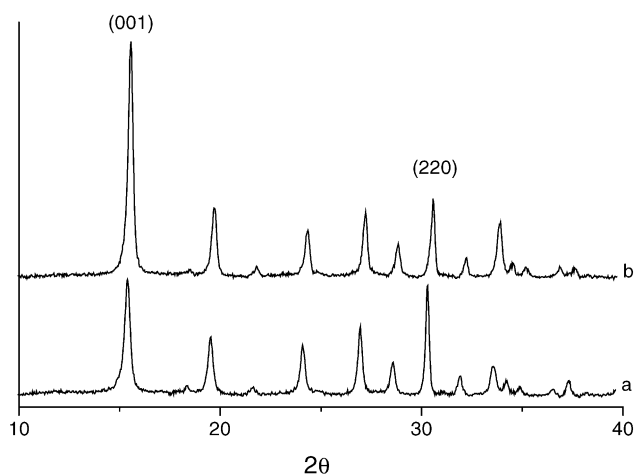


Fig. 3. Powder X-ray diffraction pattern of the doped precursor containing 1.0 mol% Ga derived from (a) Ga₂O₃ and (b) GaPO₄.

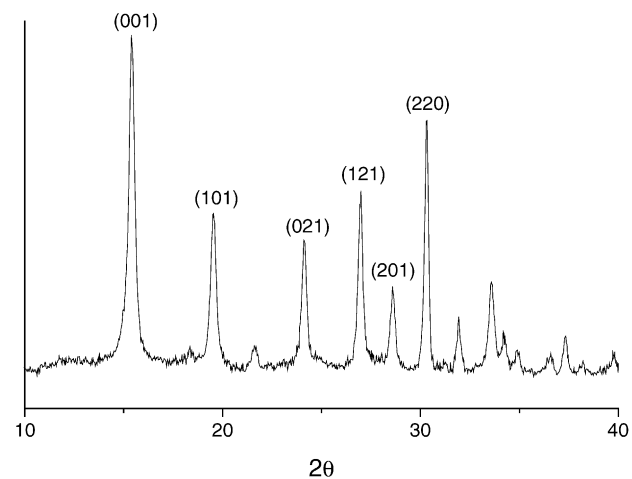


Fig. 4. Powder X-ray diffraction pattern of the precursor prepared with 1 mol% acac.

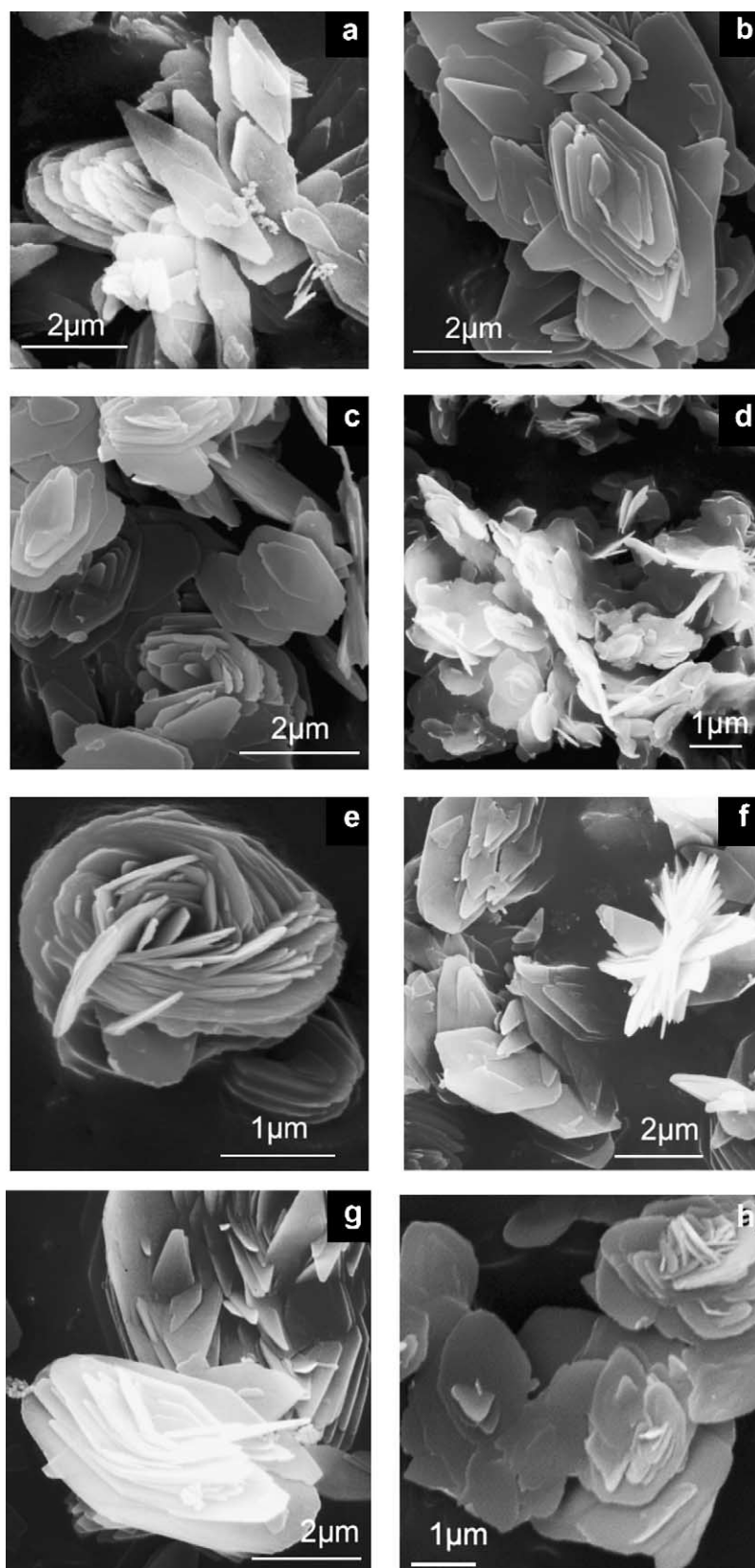


Fig. 5. Scanning electron micrographs of catalyst precursors: (a) undoped VPO; (b) 0.1% Ga derived from Ga(acac)₃; (c) 0.5% Ga derived from Ga(acac)₃; (d) 1.0% Ga derived from Ga(acac)₃; (e) 1.5% Ga derived from Ga(acac)₃; (f) 1.0% Ga derived from Ga₂O₃; (g) 1.0% Ga derived from GaPO₄ and (h) 1.0 mol% acac.

tion, the rosette often associated with the hemihydrate phase was observed. In particular, the morphology of the 0.1 mol% precursor and the undoped precursor are indistinguishable. Analysis of the materials using EDX showed that the Ga was dispersed throughout the hemihydrate crystals uniformly.

3.2. Catalyst testing and characterisation

The hemihydrate precursors were treated in situ in the laboratory microreactor with 1.6% *n*-butane in air at 400 °C. 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 1 together with the surface areas of the activated catalysts. Catalytic tests and catalyst preparations were carried out in duplicate and the data presented are fully reproducible.

The undoped catalyst and the doped catalysts prepared using Ga(acac)₃ all showed significant increases in surface area on activation. This was not observed with the Ga₂O₃, GaPO₄ and acetylacetonate derived materials.

The addition of low levels of Ga using Ga(acac)₃ as the gallium source significantly enhance the activity of the activated catalyst, in particular, the intrinsic activity (Table 1). The effect is most pronounced for the 0.1–1.0 mol% doping levels and the sample doped with 1.5 mol% Ga exhibits the same intrinsic activity as the undoped material. However, due to the enhanced surface area of this material (20 m²/g) compared to the undoped activated catalyst (15 m²/g), the catalyst performance of the doped catalyst was superior to the undoped material. A small promotion effect is also apparent for the GaPO₄-derived material. GaPO₄ prepared using the novel method was particularly inactive, and consequently, the effects on activity are not caused by materials containing GaPO₄.

The activated catalysts were characterised using powder X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The powder X-ray diffraction patterns are shown in Figs. 6–9 and all the patterns can be indexed to vanadyl pyrophosphate (VO)₂P₂O₇ although there are differences in the relative intensities of the main reflections. The materials prepared using either 1 mol% acetylacetonate or using Ga₂O₃ and GaPO₄ as the Ga source are not particularly crystalline when compared with the materials prepared using Ga(acac)₃ as the gallium source. In fact, the materials doped with 0.1–1.0 mol% Ga using Ga(acac)₃ are more crystalline than the undoped material prepared in the same way. Whereas, the 1.5 mol% doped material prepared from Ga(acac)₃ is not particularly crystalline. These differences in crystallinity may be significant in playing a role in the promotion in intrinsic activity observed for three very active materials. The Raman spectra could all assigned to (VO)₂P₂O₇ and no other phases were observed using this sensitive technique (Figs. 10–12). The morphology of the activated catalysts was investigated using scanning electron microscopy and the results are given in Fig. 13. The micro-

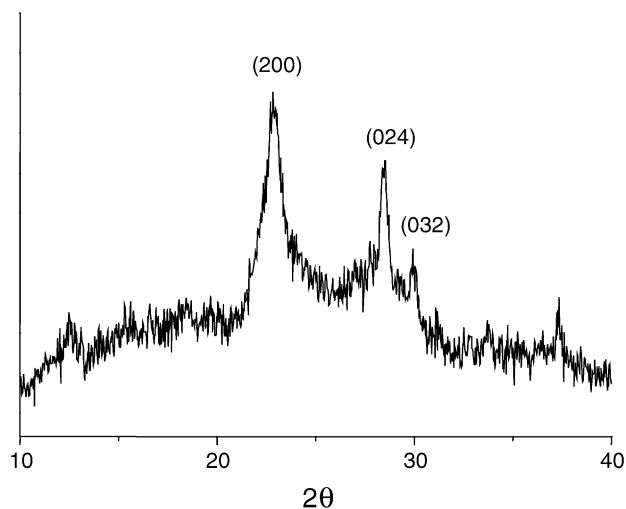


Fig. 6. Powder X-ray diffraction pattern of the undoped activated catalyst.

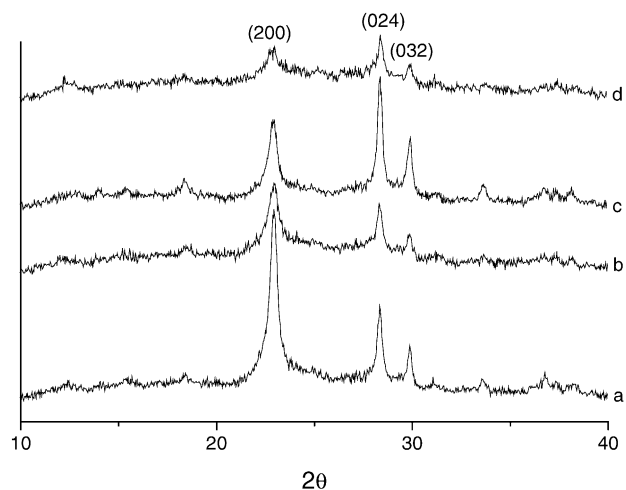


Fig. 7. Powder X-ray diffraction pattern of the doped activated catalysts derived from Ga(acac)₃: (a) 0.1% Ga; (b) 0.5% Ga; (c) 1.0% Ga and (d) 1.5% Ga.

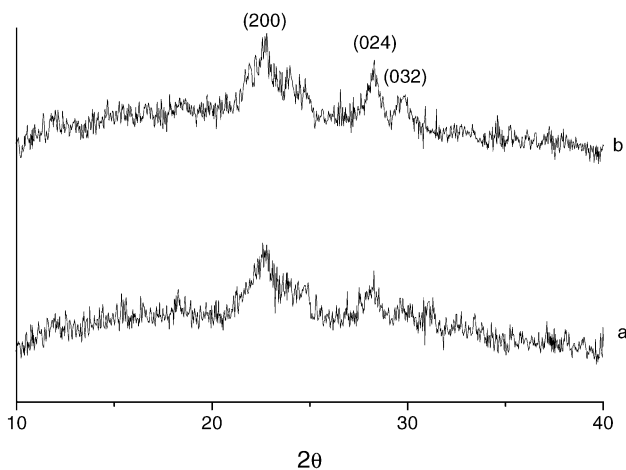


Fig. 8. Powder X-ray diffraction pattern of the doped activated catalyst containing 1.0 mol% Ga derived from (a) Ga₂O₃ and (b) GaPO₄.

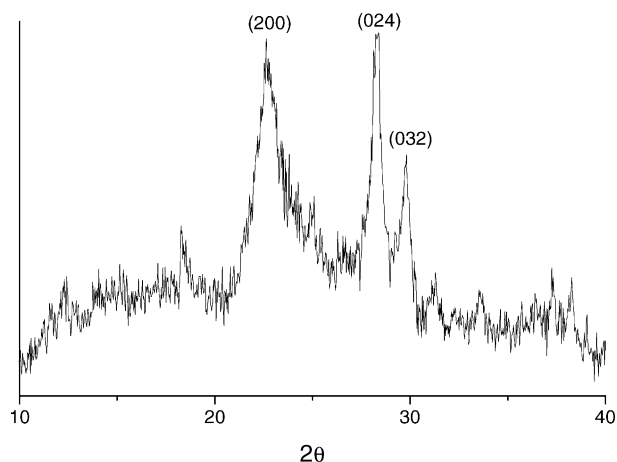


Fig. 9. Powder X-ray diffraction pattern of the activated catalyst prepared with 1 mol% acac.

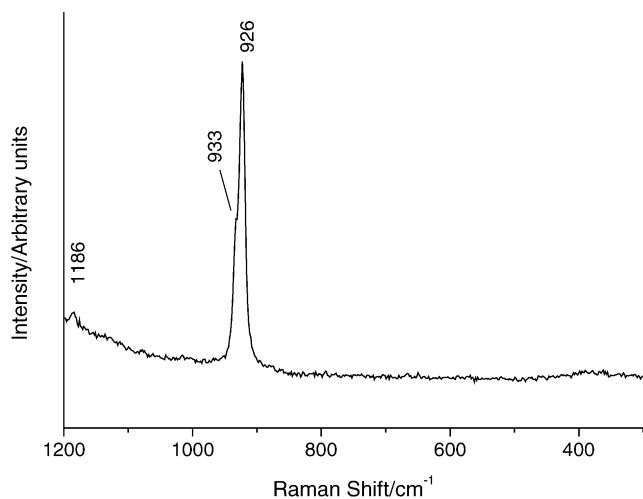


Fig. 10. Laser Raman spectra of activated catalyst derived from the undoped precursor.

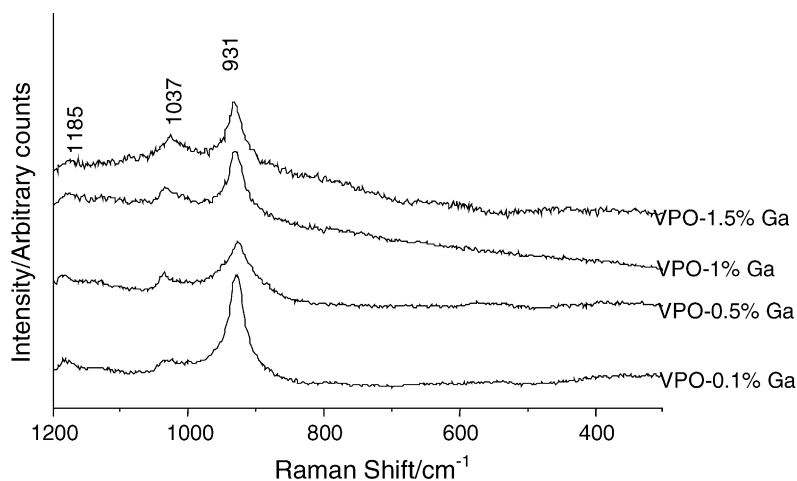


Fig. 11. Laser Raman spectra of activated catalysts derived from doping with $\text{Ga}(\text{acac})_3$.

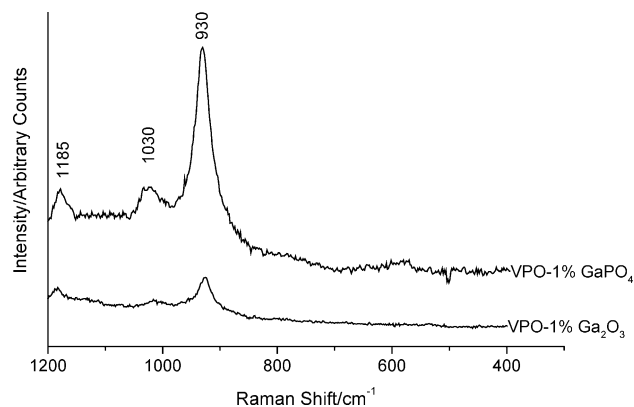


Fig. 12. Laser Raman spectra of activated catalysts derived from doping with Ga_2O_3 and GaPO_4 .

graphs shown are fully representative of the morphology of the samples. In particular, the doped materials that all display an enhancement in the intrinsic activity (Table 1), namely 0.1, 0.5 and 1.0 mol% Ga-doped activated catalysts derived from $\text{Ga}(\text{acac})_3$ and the 1.0 mol% Ga-doped activated catalyst derived from GaPO_4 , all showed platelet morphology in which the individual crystals are all relatively distinct. Whereas the doped materials with similar intrinsic activity to the undoped activated catalyst all display a rosette type morphology of arrays of platelets.

It is apparent that there are two promotion effects resulting from the addition of Ga to the vanadium phosphorus catalyst. First, the increase in surface area observed for the Ga-promoted activated catalysts derived from $\text{Ga}(\text{acac})_3$ gives rise to the standard structural promotion often observed on addition of metal cations to the vanadium phosphorus catalyst [5,6]. Second, the enhancement in intrinsic activity that is most pronounced for the 0.1–1.0 mol% Ga activated catalysts derived from $\text{Ga}(\text{acac})_3$ indicates that Ga is either acting as an electronic promoter affecting the oxidation state of the activated catalyst surface or it is introducing defects,

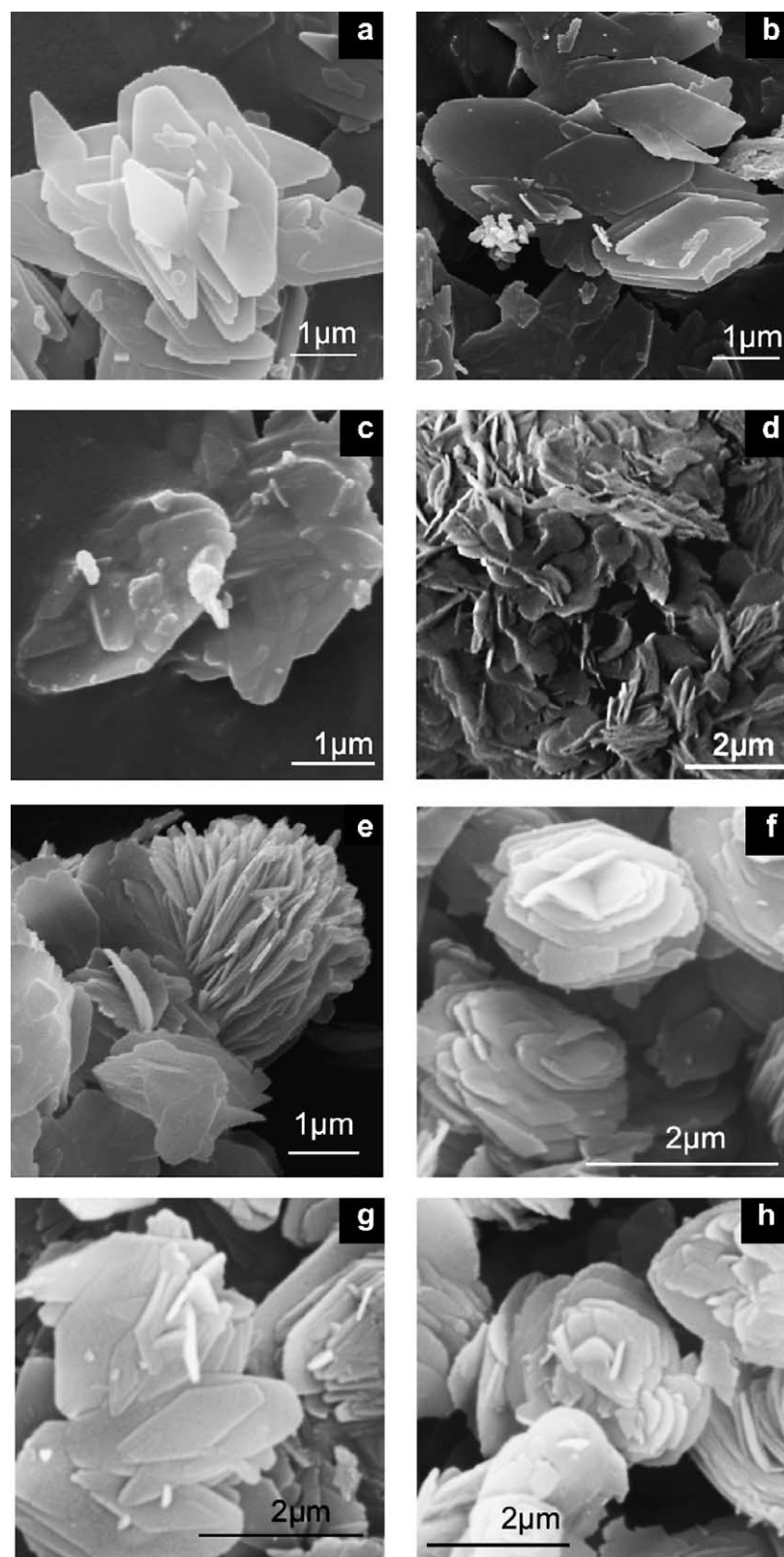


Fig. 13. Scanning electron micrographs of activated catalysts: (a) undoped VPO; (b) 0.1% Ga derived from $\text{Ga}(\text{acac})_3$; (c) 0.5% Ga derived from $\text{Ga}(\text{acac})_3$; (d) 1.0% Ga derived from $\text{Ga}(\text{acac})_3$; (e) 1.5% Ga derived from $\text{Ga}(\text{acac})_3$; (f) 1.0% Ga derived from Ga_2O_3 ; (g) 1.0% Ga derived from GaPO_4 and (h) 1.0 mol% acac.

due to the substitution of VO^{2+} by Ga^{3+} . To determine the nature of the promotion effect of Ga on the vanadium phosphate catalyst a detailed study using EXAFS, HREM and ^{31}P NMR spectroscopy combined with electrical conductivity measurements, and these findings will be published separately [17].

In conclusion this study has shown that Ga^{3+} can promote the activity of vanadium phosphate catalysts for the selective oxidation of *n*-butane to maleic anhydride. Ga^{3+} acts as both a structural and an electronic promoter. The source of the Ga^{3+} is important and for the 1 mol% Ga^{3+} doping level the best results were observed with $\text{Ga}(\text{acac})_3$ derived materials and the order of effect on the intrinsic activity is: $\text{Ga}(\text{acac})_3 > \text{GaPO}_4 > \text{Ga}_2\text{O}_3 \sim$ undoped VPO.

Acknowledgements

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