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Preparation of vanadium phosphate catalysts using water as solvent

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Abstract

The synthesis of vanadium phosphorus oxide catalysts for the selective oxidation of *n*-butane using V_2O_4 as a starting material with water as solvent is described. In the absence of added water, V_2O_4 and either H_3PO_4 or $H_4P_2O_7$ react at 145 °C to form well crystalline $VOHPO_4{\cdot}0.5H_2O$. The surface area of the precursor is significantly enhanced when water is added as a solvent. On activation in *n*-butane/air the catalyst surface area is increased from ca. $4\,m^2/g$ for the precursor to $10–13\,m^2/g$. The catalytic performance data in terms of *n*-butane conversion and maleic anhydride selectivity, is comparable to other non-promoted vanadium phosphate catalysts.

Keywords: *n*-Butane oxidation; Vanadium phosphate catalysts; V_2O_4 reaction with H_3PO_4; $VOHPO_4{\cdot}0.5H_2O$; $(VO)_2P_2O_7$

1. Introduction

Vanadium phosphate catalysts prepared from the precursor $VOHPO_4{\cdot}0.5H_2O$ represent a commercially significant class of materials. The catalysts, which are used commercially for the selective oxidation of *n*-butane [1–5], comprise a combination of $(VO)_2P_2O_7$ and $VOPO_4$ phases. It is obtained from the precursor by in situ pre-treatment with 1.5% *n*-butane in air at 400 °C [6,7]. The transformation of $VOHPO_4{\cdot}0.5H_2O$ to $(VO)_2P_2O_7$ and α_{II}-, δ-$VOPO_4$ occurs topotactically and the topotactic relationships have been reported [7]. Consequently careful preparation of the precursor $VOHPO_4{\cdot}0.5H_2O$ is the key to obtaining an effective catalyst [1–7]. The preparation of high activity catalysts has therefore become a major theme for investigations [8–22]. In general, the catalyst precursor is synthesised by the reaction of V_2O_5 and H_3PO_4 with a reducing agent and a solvent. A large number of reducing agents and solvents have been utilised for the preparation of $VOHPO_4{\cdot}0.5H_2O$. Early methods [5] used water with aqueous hydrochloric acid as the reducing agent. Methods using water as solvent have suffered from two distinct disadvantages. First, only low area catalysts are obtained, typically $1–3\,m^2/g$, and consequently only low activity catalysts are formed since in the selective oxidation of *n*-butane to maleic anhydride the catalyst activity is directly proportional to the surface area. Second, an impurity phase is formed, $VO(H_2PO_4)_2$, which is known to have poor selectivity for maleic anhydride [23]. Although the $VO(H_2PO_4)_2$ impurity can be removed using a water extraction step [23] the catalyst formed after water washing remain low area materials (typically ca. $4\,m^2/g$). A number of subsequent studies [8,11,14] have used alcohols as solvent and reducing agents and in general these methods give high surface area catalysts (ca. $20\,m^2/g$). Recently, we have

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shown that $VOPO_4{\cdot}2H_2O$ can be reduced by alcohols to form $VOHPO_4{\cdot}0.5H_2O$, and this method gives high area catalysts with controlled morphology [14].

To date, there has been very little interest in using water as solvent or trying to develop solvent-free methods. We have reported a solvent-free preparation of a V^{5+} vanadium phosphate [24], but the material demonstrated poor selectivity for maleic anhydride. In this paper we present our initial results on solvent-free and water-based preparations for the synthesis of $VOHPO_4{\cdot}0.5H_2O$ using V_2O_4 as the starting material and show that catalysts with comparable activity and selectivity to the standard alcohol solvent methods can be prepared.

2. Experimental

2.1. Catalyst preparation

Vanadium phosphate catalyst precursors were prepared using V_2O_4 as follows: V_2O_4 (5.9 g, Strem, 99%) and H_3PO_4 (6.7 g, Aldrich, 99%) were heated together in an autoclave, in the absence of any added water, at 145 °C for 72 h. Following the reaction, the solid produced was recovered by filtration, washed with distilled water (50 ml) and dried in air (120 °C, 16%) and this catalyst precursor is denoted VPO_{P1}. A second precursor was prepared in the same way but using $H_4P_2O_7$ (6.2 g, Aldrich, 99%) as the phosphorus source. This catalyst was denoted VPO_{P2}. VPO_{P1} and VPO_{P2} were refluxed with distilled water (20 ml/g solid) for 2 h. The solid was recovered by filtration when hot, washed with distilled water (50 ml) and dried in air (120 °C, 16 h). These precursors are denoted VPO_{P3} and VPO_{P4}, respectively. A further set of precursors were prepared in an analogous manner except distilled water (20 ml) was added to the autoclave prior to heating at 145 °C for 22 h. These precursors are denoted VPO_{P5} ($V_2O_4 + H_3PO_4$), VPO_{P6} ($V_2O_4 + H_4P_2O_7$), VPO_{P7} (VPO_{P5} refluxed with water and filtered hot) and VPO_{P8}(VPO_{P6} refluxed with water and filtered hot).

Two other precursors were prepared as comparative materials. A precursor was prepared according to the VPA method using water as a solvent [19]. V_2O_5 (6.06 g, Strem, 99%) was refluxed in aqueous HCl (37% by volume, 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 [16] V_2O_5 (11.8 g, Strem, 99%) and H_3PO_4 (15.5 g, Aldrich, 85 vol.%) were refluxed in water (24 ml/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 [19]. 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).

2.2. Catalyst testing and characterisation

The oxidation of *n*-butane was carried out using a microreactor containing a standard volume of catalyst (0.5 ml). Prior to use, the catalysts were pelleted and sieved to give particles (200–300 μm in diameter). *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 ≥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 (400 °C, GHSV $= 2500\,h^{-1}$) 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 catalytic 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 ($\lambda = 514.532$). 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.

3. Results and discussion

The eight precursor samples were prepared using V_2O_4 as the starting materials. They were characterised by powder X-ray diffraction (Fig. 1) and were found to comprise solely of $VOHPO_4{\cdot}0.5H_2O$. Raman spectroscopy confirmed that no other vanadium phosphate phases were present. Interestingly, no traces of $VO(H_2PO_4)_2$ were observed to be present in the prepared precursors both before and after the water washing treatment. This was even the case for the preparations in which no additional water was added to the autoclave (i.e. VPO_{P1} and VPO_{P2}). During the synthesis of $VOHPO_4{\cdot}0.5H_2O$ in the autoclave at 145 °C water is formed as a by-product when H_3PO_4 is used as phosphorus source (VPO_{P1}):

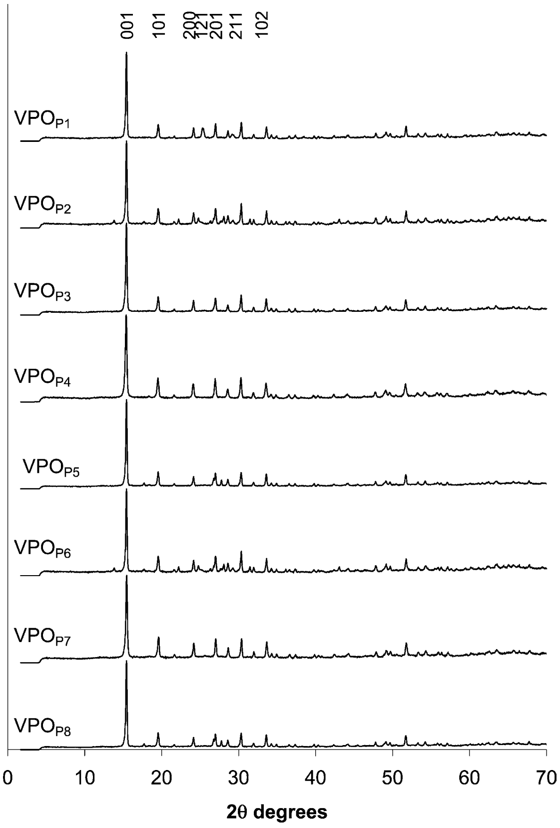

Fig. 1. The powder XRD patterns of the catalyst precursors.

$$V_2O_4 + 2H_3PO_4 \rightarrow 2VOHPO_4 \cdot 0.5H_2O + H_2O$$

But not when $H_4P_2O_7$ is used as phosphorus source (VPO_{P2}):

$$V_2O_4 + H_4P_2O_7 \rightarrow 2VOHPO_4 \cdot 0.5H_2O$$

It is therefore concluded that this synthesis pathway is very specific and the deleterious by-product $VO(H_2PO_4)_2$ is not formed. Of course, when water is formed during the synthesis, or when present as a solvent, any $VO(H_2PO_4)_2$ would be expected to remain in solution since it is highly soluble in water and the samples were recovered by hot filtration.

The surface areas of the two precursors formed in the presence of added water (VPO_{P5}, VPO_{P6}) were found to be very similar, ca. 4 m^2/g. On heating in water at 100 °C for 2 h the surface area was not affected markedly. This is considered to be consistent with the observation that no soluble impurities were present in the precursors.

The precursors were used as catalysts of the oxidation of *n*-butane (1.7% *n*-butane in air, gas hourly space velocity 2500 ml gas/(ml catalyst h)) at 400 °C. During this time the catalyst performance for the formation of maleic anhydride steadily improved (Fig. 2) until a steady state performance was achieved. The catalysts obtained from the precursors $VPO_{P1–8}$ are denoted $VPO_{C1–8}$, respectively. The data at steady state are summarised in Table 1, and data are also given for the materials prepared using the standard VPA and VPD methods. It is apparent that the final surface areas of the materials prepared from V_2O_4 and H_3PO_4 or $H_4P_2O_7$ in an autoclave at 145 °C are much higher than those previously found using aqueous methods. In particular, the surface area for when aqueous HCl is used as a solvent and reducing agent is only 1.5–4 m^2/g, whereas with methods based on V_2O_4 surface areas of 10–13 m^2/g can be obtained. The materials prepared in the absence of added water from V_2O_4/H_3PO_4 (VPO_{C1} derived from VPO_{P1}) and $V_2O_4/H_4P_2O_7$ (VPO_{C2} derived from VPO_{P2}) gave lower surface areas, 4 and 7 m^2/g, respectively. Both gave significantly higher surface areas when the precursors were treated with water prior to catalyst testing. The increase in surface area produces a marked increase in the conversion of butane. For the catalysts prepared in aqueous solution, the surface areas and butane conversion do not increase when treated with water prior to testing. Indeed the performance is very similar to the material prepared in solvent-free conditions after the water reflux step.

Representative catalytic data for the catalysts prepared using H_3PO_4 are shown in Fig. 2. The material prepared without solvent (VPO_{C1}) exhibits a low conversion which is greatly enhanced after refluxing in water (VPO_{C3}), while the catalyst prepared under aqueous conditions (VPO_{C5}) does not have an improved performance when treated with water (VPO_{C7}). These results indicate the importance of water as a solvent in achieving high surface area materials.

Characterisation of the catalysts after activation was carried out using powder X-ray diffraction and the

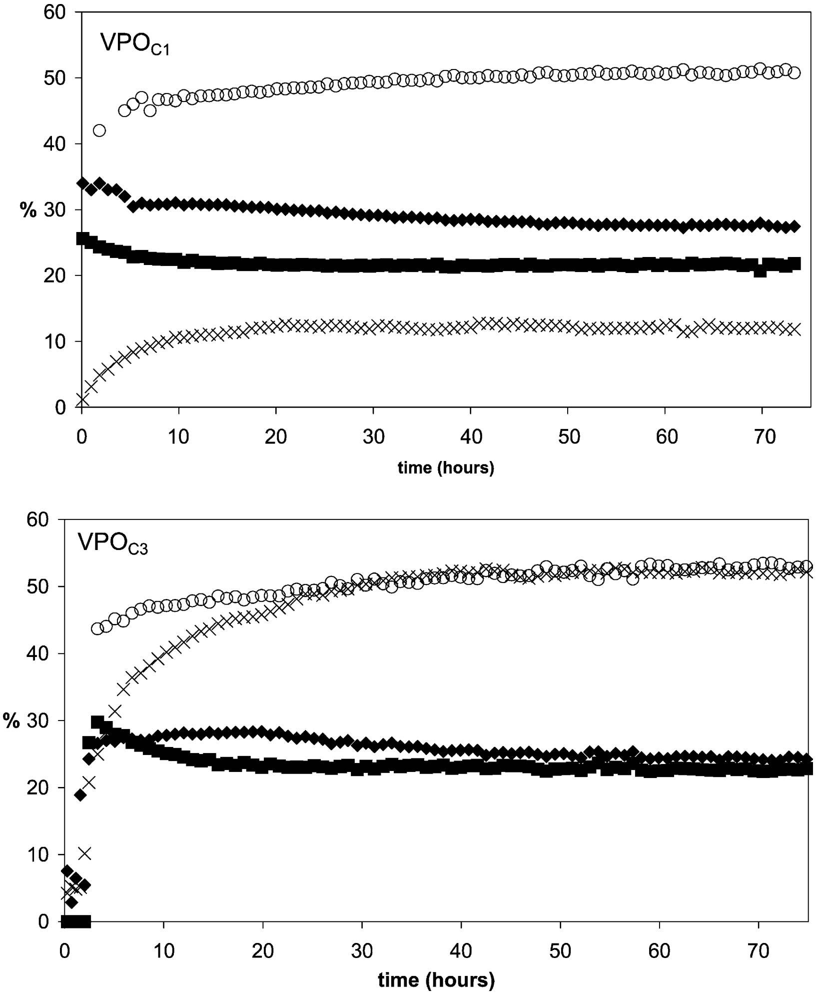

Fig. 2. Representative catalyst performance data for the catalysts prepared using V_2O_4 and H_3PO_4 as starting materials. Reaction conditions: 1.7 vol.% *n*-butane in air, 400 °C, 2500 ml gas/(ml catalyst h). (×) Conversion; (○) maleic anhydride selectivity; (◆) CO_2 selectivity; (■) CO selectivity.

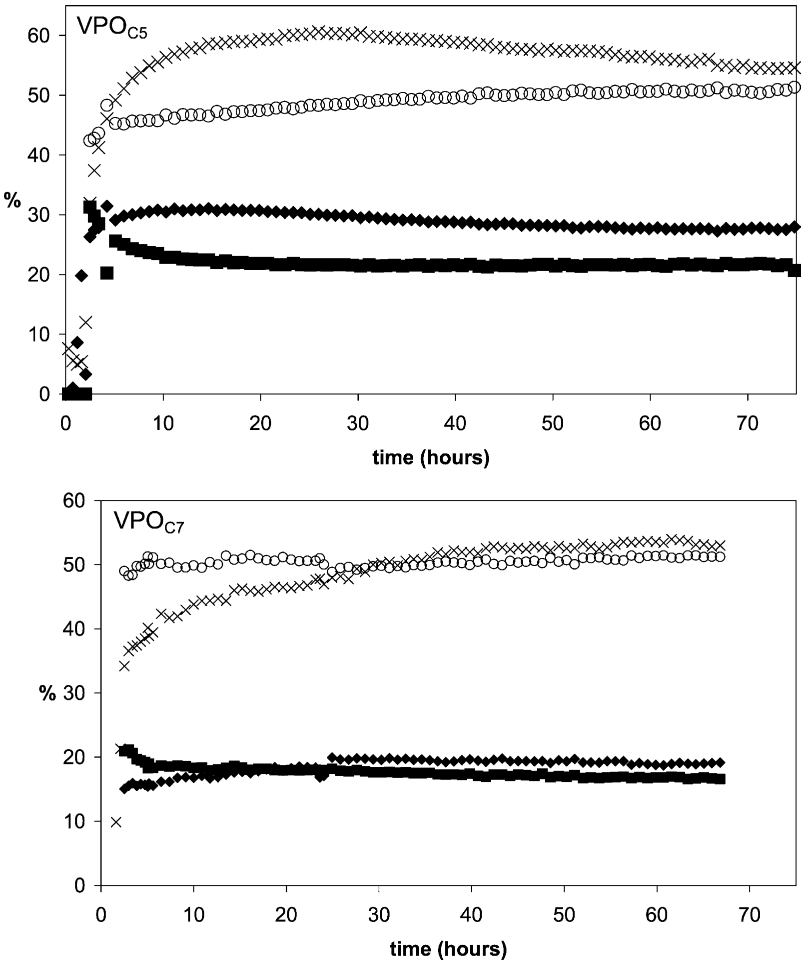

Fig. 2. (*Continued*).

Table 1
Catalyst performance of vanadium phosphorus catalysts for the oxidation of *n*-butane to maleic anhydride[a]

Catalyst	Preparation method	Surface area (m^2/g) catalyst	*n*-Butane conversion (%)	Maleic anhydride selectivity (%)	10^{-5} space time yield (mol MA/(m^2 h))
VPO_{P1}	$V_2O_4 + H_3PO_4$	4	12	50	2.34
VPO_{P2}	$V_2O_4 + H_4P_2O_7$	7	17	54	2.05
VPO_{P3}	$V_2O_4 + H_3PO_4$ + water reflux	10	53	53	4.21
VPO_{P4}	$V_2O_4 + H_4P_2O_7$ + water reflux	13	45	53	2.80
VPO_{P5}	$V_2O_4 + H_3PO_4 + H_2O$	11	55	51	3.97
VPO_{P6}	$V_2O_4 + H_4P_2O_7 + H_2O$	10	49	53	4.06
VPO_{P7}	$V_2O_4 + H_3PO_4 + H_2O$ + water reflux	13	50	51	3.04
VPO_{P8}	$V_2O_4 + H_4P_2O_7 + H_2O$ + water reflux	12	50	57	3.71
VPD	$VOPO_4 \cdot 2H_2O$ + isobutanol + water reflux	22	65	58	2.68
VPA1	$V_2O_5 + H_3PO_4 + HCl_{aq}$	1.5	4	45	1.88
VPA2	$V_2O_5 + H_3PO_4 + HCl_{aq}$ + water reflux	4	11	45	1.93

[a] Reaction conditions: 400 °C, 1.7% *n*-butane in air, GHSV: 2500 ml gas/(ml catalyst h).

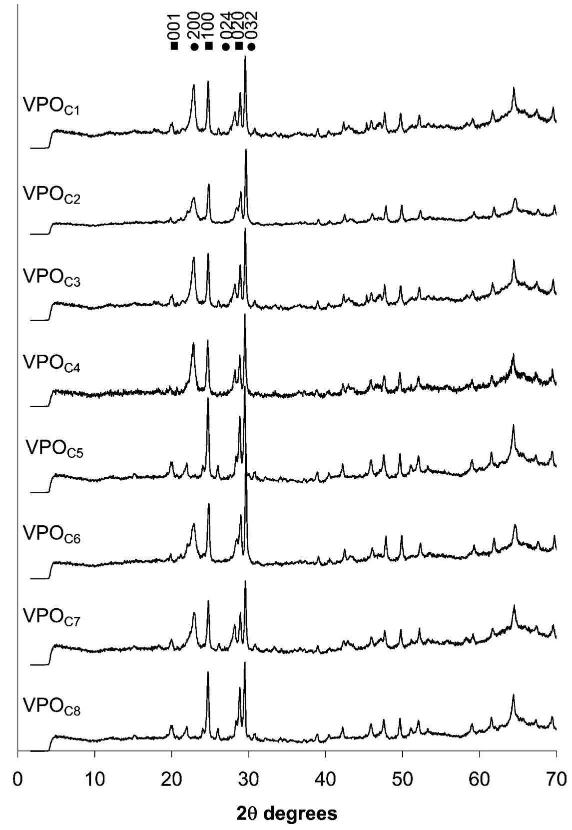

Fig. 3. The powder XRD patterns of the catalysts after testing. (●) $(VO)_2P_2O_7$; (■) α_{II}-$VOPO_4$.

patterns are shown in Fig. 3. They were all observed to be very similar and comprised $(VO)_2P_2O_7$, together with α_{II}-$VOPO_4$. Raman spectra were constant with this observation.

The selectivity to maleic anhydride observed for the V_2O_4-derived catalysts was similar to other non-promoted VPO catalysts reported in the literature. However, at present the surface area achieved for the final catalyst is typically 10–13 m^2/g. Although this is higher than other aqueous solvent preparations previously reported [23], they are still low compared with the surface areas that can be achieved from the use of alcohols as solvents (typically >20 m^2/g). However, the space time yield of the materials prepared using the aqueous method with V_2O_4 is higher than that of catalysts prepared using alcohol as solvent (Table 1). Although it is considered unlikely that V_2O_4 would be used as a starting material for the synthesis of commercial vanadium phosphate catalysts, the present study does show that relatively high area catalysts can be achieved using water as solvent. At present our initial experiments have only used an autoclave temperature of 145 °C and a 3-day preparation time. However, significant improvements can be expected for the catalyst surface area if the reaction conditions are optimised with water as a solvent. Our present study also shows that solvent-free methods can also be developed using the autoclave methodology and this may be of value in the synthesis of novel formulations or promoted vanadium phosphate catalysts.

Acknowledgements

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