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RESEARCH NOTE

The Unexpected Role of Aldehydes and Ketones in the Standard Preparation Method for Vanadium Phosphate Catalysts

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$VO(H_2PO_4)_2$ is formed as the exclusive product from the reaction of aldehydes or ketones with V_2O_5 and H_3PO_4 whether aqueous (85%) or crystalline (100%) orthophosphoric acid is used. This exclusive product formation has been observed with a broad range of aldehydes and ketones (C_4–C_{10}). This finding casts doubt on the current commercial preparation of vanadium phosphate catalysts used for the oxidation of *n*-butane to maleic anhydride. This catalyst is derived from a crystalline precursor $VOHPO_4 \cdot 0.5H_2O$, formed from the reaction of V_2O_5 and H_3PO_4 with an alcohol. The alcohol acts as a reducing agent forming an aldehyde or ketone. These aldehydes and ketones, once formed, will lead to the formation of $VO(H_2PO_4)_2$ as an impurity, at levels which will be difficult to detect but which are known to affect catalytic performance adversely. The use of isobutanol containing a small quantity of butanone for the reaction of V_2O_5 and H_3PO_4 (100%) confirmed that low levels of $VO(H_2PO_4)_2$ can be formed together with $VOHPO_4 \cdot 0.5H_2O$.

Key Words: **vanadium phosphate catalyst preparation; $VO(H_2PO_4)_2$; butane oxidation to maleic anhydride.**

INTRODUCTION

Vanadium phosphate compounds are used extensively as heterogeneous catalysts for the production of maleic anhydride for *n*-butane partial oxidation. As a result, vanadium phosphates and their preparation have been extensively studied (1, 2). The preferred industrial catalyst is synthesised from $VOHPO_4 \cdot 0.5H_2O$ to form an active catalyst comprising $(VO)_2P_2O_7$ with α_{II}-, γ-, and δ-$VOPO_4$ by *in situ* activation in *n*-butane/air (3). A major breakthrough in the synthesis of $VOHPO_4 \cdot 0.5H_2O$ was pioneered by Johnson *et al.* (4) and involves the reaction of V_2O_5 with H_3PO_4 under reflux with an alcohol as a reducing agent. When the alcohol is used as a reducing agent it is oxidised to form an aldehyde or ketone (4). This method superseded the use of aqueous HCl or HCl dissolved in alcohols as reducing agents (2), and this method can now be considered as the standard industrial preparation method. Most researchers agree that it is essential that the desired precursor $VOHPO_4 \cdot 0.5H_2O$ is produced in as pure a form as possible. In particular, it is known that the material $VO(H_2PO_4)_2$ can be deleterious when present as an impurity in the catalyst precursor since it lowers the surface area of the activated catalyst and consequently these catalysts display poorer catalyst performance. While the use of alcohols as reducing agents has been extensively studied (1, 5, 6), to date no attention has been given to the potential role played by the aldehyde or ketone by-products. We have now addressed this aspect of catalyst synthesis and have found that, surprisingly, the use of aldehydes and ketones leads to the exclusive synthesis of $VO(H_2PO_4)_2$ which has previously been shown by itself to exhibit poor catalytic performance (7, 8), and when present with $VOHPO_4 \cdot 0.5H_2O$ can significantly impair (9) the function of the catalyst for the oxidation of *n*-butane.

METHODS

V_2O_5 (1.0 g, Strem) and H_3PO_4 (2.8 g, 85% Aldrich) were refluxed with an aldehyde/ketone (40 ml, Aldrich) for 16 h. The resultant pale blue solid was recovered by vacuum filtration, washed with the aldehyde/ketone (50 ml) and acetone (50 ml), and dried in air (110°C, 24 h). Additional experiments were conducted using crystalline H_3PO_4. V_2O_5 (1.0 g, Strem) and H_3PO_4 (2.4 g, 100% Fischer) refluxed with isobutanol, isobutanol/butanone, and butanone (40 ml, Aldrich) for 16 h. The resultant pale blue solid was recovered by vacuum filtration, washed with the alcohol/ketone (50 ml), and dried in air (110°C, 24 h).

In a similar set of experiments $VOPO_4 \cdot 2H_2O$ (1.0 g) prepared by standard methods (6) was reacted with H_3PO_4 (0.059 g, 85% Aldrich) under reflux with the aldehyde/ketone (40 ml, Aldrich) for 16 h. The product

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was recovered by filtration and washed with the aldehyde/ketone (50 ml) and acetone (50 ml) and dried in air (110°C, 24 h).

Powder X-ray diffraction was performed using an Enraf Nonius FR590 X-ray generator with a CuK_α source fitted with an Inel CPS 120 hemispherical detector. Laser Raman spectra were obtained using a Renishaw Ramanscope spectrograph fitted with a green Ar^+ laser ($\lambda = 514.532$ nm). Thermalgravimetric analysis was performed using a Perkin Elmer TGA 7 instrument.

Vanadium phosphates were tested for the oxidation of *n*-butane with air in a standard laboratory microreactor. Butane and air were fed to the reactor using calibrated mass flow controllers and the mixture (1.5 vol% butane in air) was passed over the heated catalyst (0.5 g). The exit lines from the reactor were heated and the products were analysed using on-line gas chromatography.

RESULTS AND DISCUSSION

In the first set of experiments the reaction of V_2O_5 and H_3PO_4 (85%) was investigated using aldehydes and ketones in place of an alcohol. In this way the standard method of preparation has been modified to use an aldehyde and ketone. Since aldehydes and ketones are not expected to act as a reducing agent most researchers would consider that no reaction would be anticipated. However, a rapid reaction was observed and the exclusive product was observed to be $VO(H_2PO_4)_2$ from the full range of C_4–C_{10} aldehydes and ketones investigated. The powder X-ray diffraction patterns and laser Raman spectra for typical samples of $VO(H_2PO_4)_2$ are shown in Fig. 1. These diffraction and spectral data are in full agreement with those published previously for $VO(H_2PO_4)_2$ (10, 11). A subsequent set of experiments was carried out using crystalline H_3PO_4 (100%), the starting material that is often used in commercial catalyst preparation, using butanone. Again, $VO(H_2PO_4)_2$ was formed as the only isolated reaction product (Fig. 2a) indicating that the water (added in the form of 85% H_3PO_4) is not the reason for the formation of $VO(H_2PO_4)_2$. Indeed water is formed during the reaction between V_2O_5 and H_3PO_4 during the alcoholic reduction at levels which are fully miscible with the reaction mixtures. We consider that this method, therefore, represents a novel and general synthetic route for the synthesis of high purity $VO(H_2PO_4)_2$. The catalyst performance of $VO(H_2PO_4)_2$ prepared in this way for the oxidation of *n*-butane was investigated and the results are shown in Table 1. It is clear that the activated material is not particularly active and poor selectivity to maleic anhydride is observed.

In a further set of experiments, the reaction of V_2O_5 with H_3PO_4 (100%) in isobutanol and butanone mixtures (2 and 10 mol%) was investigated. The powder X-ray diffraction pattern of the resulting materials show that $VOHPO_4 \cdot 0.5H_2O$ is produced together with $VO(H_2PO_4)_2$ as a minor phase (Fig. 2a). Thermalgravimetric analysis confirmed this finding (Fig. 2b). Pure $VO(H_2PO_4)_2$ shows a weight loss at ca. 400–420°C whereas $VOHPO_4 \cdot 0.5H_2O$ transforms to $(VO)_2P_2O_7$ at ca. 480°C (2). It is clear that the pure materials show only a single weight loss whereas the materials formed from the reaction with isobutanol/butanone mixtures exhibit two distinct weight losses. These results show that small amounts of the ketone can lead to the formation of $VO(H_2PO_4)_2$ as a detectable impurity.

In previous studies (5, 6), we have shown that $VOPO_4 \cdot 2H_2O$ can be reduced with alcohols to form $VOHPO_4 \cdot 0.5H_2O$ and this method also leads to the formation of an aldehyde/ketone. Hence, in a subsequent set of experiments, we investigated the potential role of aldehydes and ketones in this synthetic method. In this case, for all simple aldehydes and ketones studied no reaction was observed with $VOPO_4 \cdot 2H_2O$. This indicates that this preparation method may be the preferred route for pure samples of the hemihydrate precursor. However, addition of a small amount of H_3PO_4 (molar ratio: $VOPO_4 \cdot 2H_2O : H_3PO_4 = 1:0.1$) led to the synthesis of $VO(H_2PO_4)_2$ for all aldehydes/ketones investigated and the X-ray diffraction patterns were similar to those shown in Fig. 1a. This observation leads us to suggest that the aldehyde/ketone acts as a reducing agent via its enol tautomer, the concentration of which is promoted by the addition of a Brønsted acid. Some ketones, notably β-diketones, exist mainly in the enol form.

TABLE 1

Oxidation of *n*-Butane over $VO(H_2PO_4)_2$

Aldehyde/ketone	Surface area final catalyst ($m^2\,g^{-1}$)	*n*-Butane conversion (%)	Selectivity (%) MA	CO	CO_2	Specific activity (10^{-5} mol m^{-2} h^{-1})
Octanal	1.3	21.1	25	45	30	2.67
2-Octanone	1.9	21.6	25	47	28	1.92
3-Octanone	0.9	16.4	25	43	32	2.98
Butanone	1.7	28.5	22	53	25	2.45
2-Hexanone	1.0	8.5	28	37	35	1.60

Note. Reaction conditions, 385°C, 1.5% *n*-butane in air, GHSV = 1000 h^{-1}.

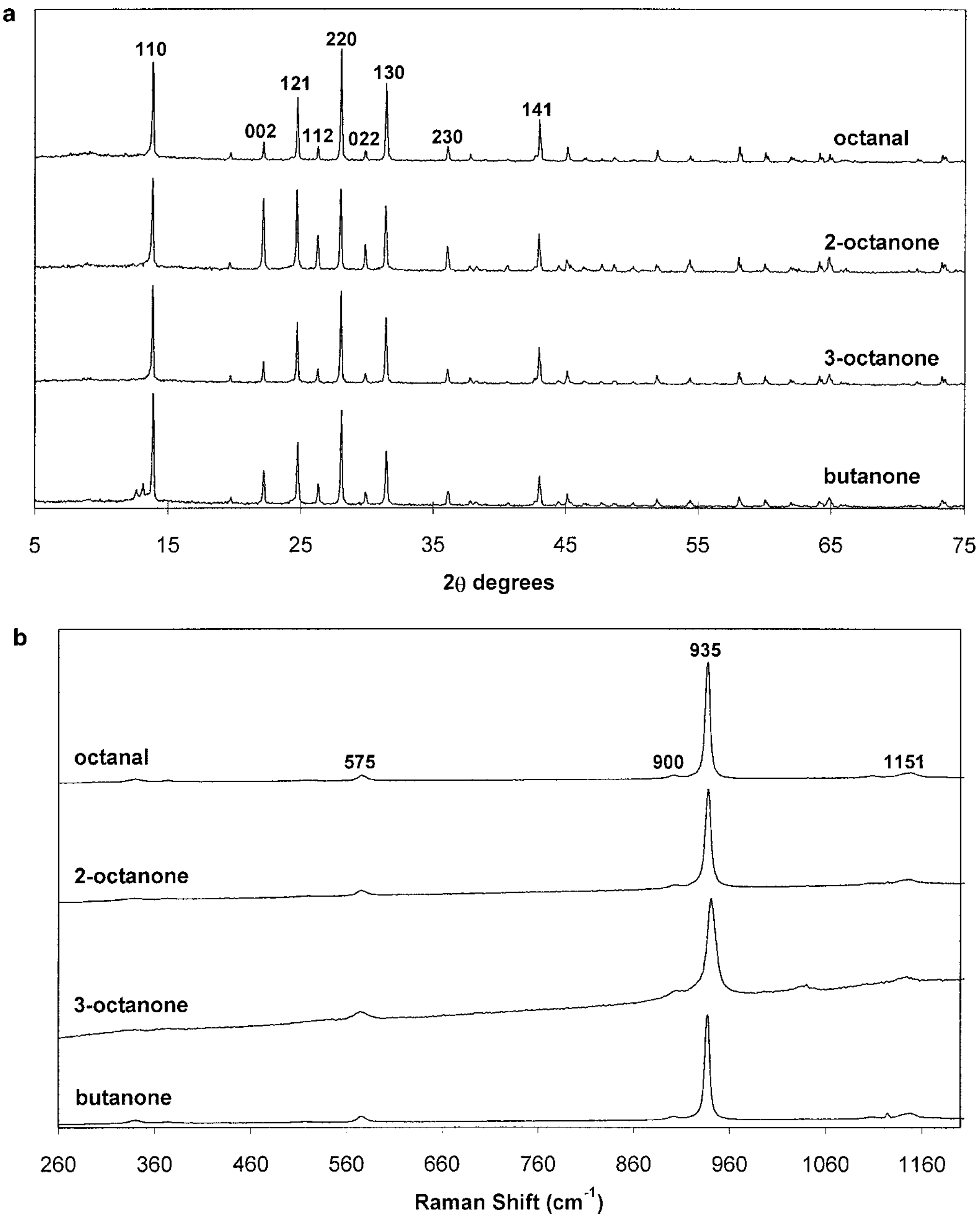
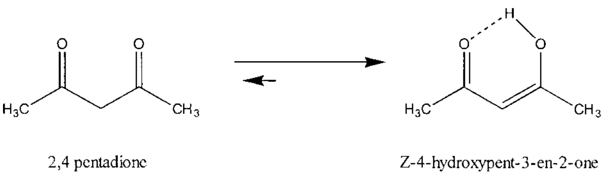


FIG. 1. (a) Powder X-ray patterns for $VO(H_2PO_4)_2$ prepared from the reaction of V_2O_5 (85%) with representative aldehydes/ketones as reducing agents. The patterns are indexed fro $VO(H_2PO_4)_2$. (b) The Raman spectra of $VO(H_2PO_4)_2$ prepared using aldehydes/ketones as reducing agents (literature values (11): 1151 cm^{-1}, br, m; 935 cm^{-1}; vs; 575 cm^{-1}; m).

For example, 2,4-pentadione is stabilised in the enol form by the conjugated enone and formation of an intramolecular hydrogen bond:



To demonstrate that ketones/aldehydes act as reducing agents in their enol form in the formation of $VO(H_2PO_4)_2$, $VOPO_4 \cdot 2H_2O$ was refluxed with 2,4-pentadione for 16 h in the absence of H_3PO_4 and $VO(H_2PO_4)_2$ was formed as the exclusive product.

The observation that $VO(H_2PO_4)_2$ can be readily formed from V_2O_5 and H_3PO_4 (85% or 100%) in a one-step synthesis using aldehydes and ketones is of significance for the synthesis of the commercially important hemihydrate

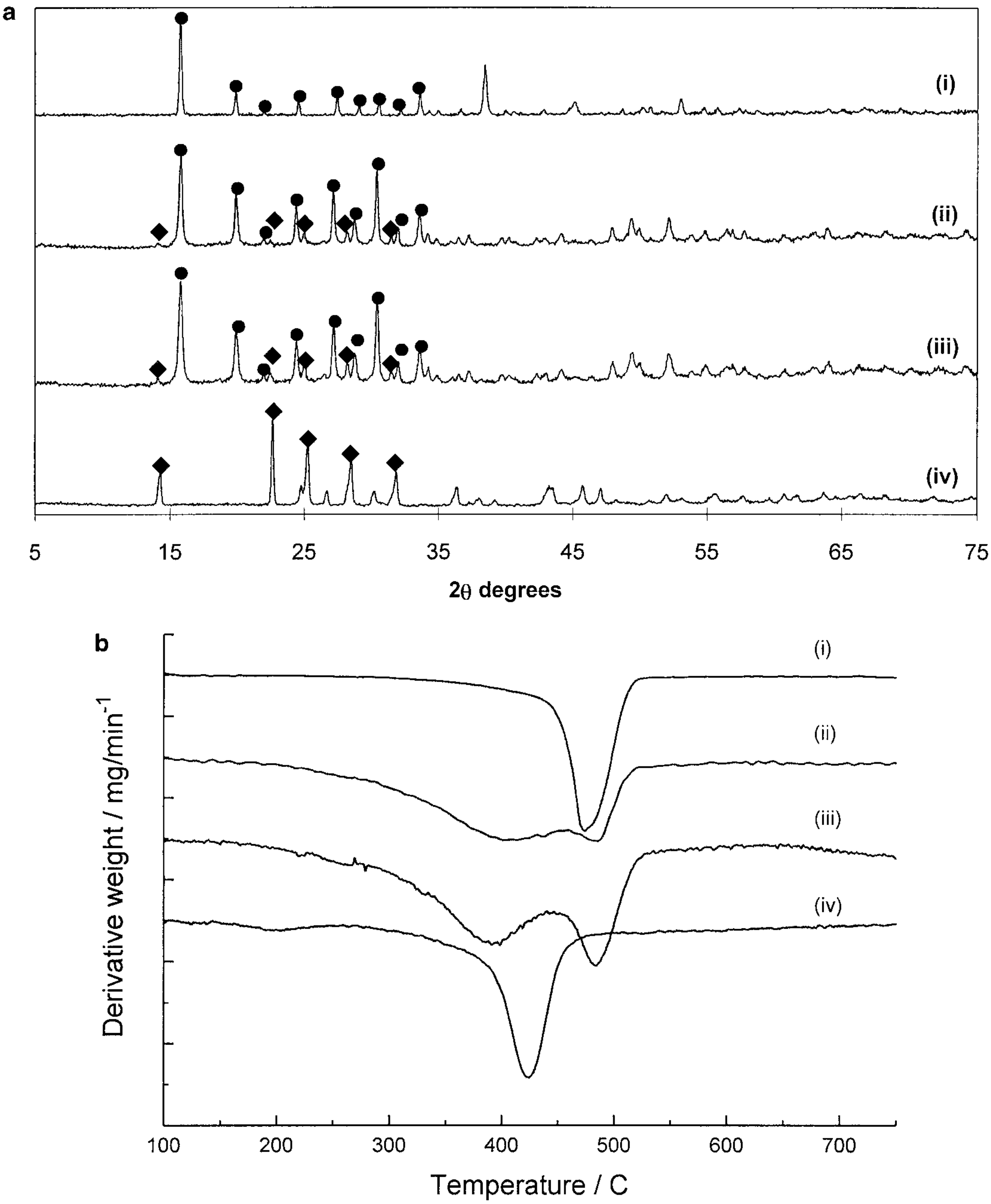
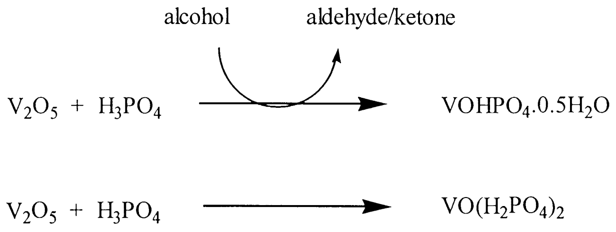


FIG. 2. (a) Powder X-ray diffraction patterns of the material from the reaction of V_2O_5 with H_3PO_4 (100%) using isobutanol/butanone mixtures: (i) 100% isobutanol, (ii) 98% isobutanol and 2% butanone, (iii) 90% isobutanol and 10% butanone, and (iv) 100% butanone. Key: ● reflections assigned to $VOHPO_40.5H_2O$; ◆ reflections assigned to $VO(H_2PO_4)_2$. (b) Thermalgravimetric analysis of the material from the reaction of V_2O_5 with H_3PO_4 (100%) using isobutanol/butanone mixtures: (i) 100% isobutanol, (ii) 98% isobutanol and 2% butanone, (iii) 90% isobutanol and 10% butanone, and (iv) 100% butanone.

$VOHPO_4 \cdot 0.5H_2O$ precursor. The hemihydrate is typically synthesised from V_2O_5 and H_3PO_4 using an alcohol as the reducing agent (1, 5, 6) which leads to the formation of aldehydes/ketones as by-products (4). Invariably, this will lead potentially to the formation of $VO(H_2PO_4)_2$ as a by-product, albeit in trace amounts. Indeed, we have demonstrated this experimentally.



$VO(H_2PO_4)_2$ exhibits poor performance for the oxidation of *n*-butane (7, 8) and additionally we have previously shown (5, 9) that trace impurities of $VO(H_2PO_4)_2$ in $VOHPO_4 \cdot 0.5H_2O$ leads to impaired catalytic performance on activation. The trace amounts formed by the action of the aldehyde/ketone impurities in the standard $VOHPO_4 \cdot 0.5H_2O$ preparation would not be expected to be readily observed by diffraction or other characterisation methods, and so their formation may have been overlooked to date in the standard preparation method. However, if present, $VO(H_2PO_4)_2$ will lead to a lower surface area in the activated catalyst and hence lead to poorer catalyst performance. Fortunately, $VO(H_2PO_4)_2$ is readily soluble in hot water, whereas $VOHPO_4 \cdot 0.5H_2O$ is insoluble, and hence $VO(H_2PO_4)_2$ can be easily removed by a simple water extraction procedure (9). Alternatively, researchers should consider the use of the method based on the reduction of $VOPO_4 \cdot 2H_2O$ by alcohols since, in this case, the aldehyde/ketone by-product is inactive for the formation of $VO(H_2PO_4)_2$. This observation may explain the previous finding that, although catalysts prepared by the reaction of V_2O_5/H_3PO_4 or $VOPO_4 \cdot 2H_2O$ with alcohols have the same specific activity, catalysts prepared by the $VOPO_4 \cdot 2H_2O$ route can give much higher surface areas (typically >40 $m^2 g^{-1}$) when compared with the V_2O_5/H_3PO_4 route (typically 30 $m^2 g^{-1}$). In any event, the results of this study confirm that careful consideration should be given to the role of reaction by-products in the preparation of heterogeneous catalysts.

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