

Control of the Composition and Morphology of Vanadium Phosphate Catalyst Precursors from Alcohol Treatment of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

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The composition and the morphology of vanadium phosphate catalyst precursors is shown to be controlled by the choice of the alcohol selected to carry out the dehydration and reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

Vanadium phosphate catalysts have been extensively studied for over 25 years since Bergmann and Frisch¹ disclosed they were effective catalysts for the selective oxidation of *n*-butane to maleic anhydride. One reason for this interest is that they represent one of the few catalysts for selective alkane activation. Another reason is that vanadium phosphates can be prepared as a large number of crystalline compounds, each of which has been well characterised, e.g. $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and $(\text{VO})_2\text{P}_2\text{O}_7$.² It is considered^{3,4} that the main active phase in catalysts stabilised under reaction conditions is $(\text{VO})_2\text{P}_2\text{O}_7$ which is formed topotactically from the precursor $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ which can be prepared by a number of methods. Most methods utilise V_2O_5 and H_3PO_4 with aqueous HCl ⁵ or alcohols⁶ as reducing agents. Johnson *et al.*² demonstrated that $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ could be made by direct reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ using either ethanol or isobutanol, but interestingly no longer chain alcohols were investigated. A subsequent study by Horowitz *et al.*⁷ also investigated C_2 – C_4

alcohols and largely confirmed the work by Johnson *et al.*² We have now investigated the role of the alcohol in this preparative route and demonstrate, for the first time, that the composition and morphology of the catalyst precursor, and consequently those features of the final activated catalyst, can be effectively controlled by the choice of the alcohol, particularly for alcohols containing four or more carbon atoms.

$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was prepared by reacting V_2O_5 (5.0 g) with H_3PO_4 (30 ml, 85%) in water (120 ml) under reflux for 24 h, the yellow solid was recovered by filtration, washed with water and then acetone and dried in air at 110 °C. $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was refluxed with predried alcohols for 20 h. (50 mol alcohol/mol $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$) and the solid product was recovered by filtration then dried in air at 110 °C for 16 h. The resultant vanadium phosphate precursors were characterised by infra-red spectroscopy and X-ray diffraction. The infra-red spectra for the precursors prepared using 1- and 2- C_4 – C_8 alcohols were identical to that expected for $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, however, the X-ray diffraction patterns show consistent differences between the precursors prepared using the 1- and 2-alcohols (Fig. 1). Precursors prepared from 1-alcohols comprise $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ crystals for which the [220]

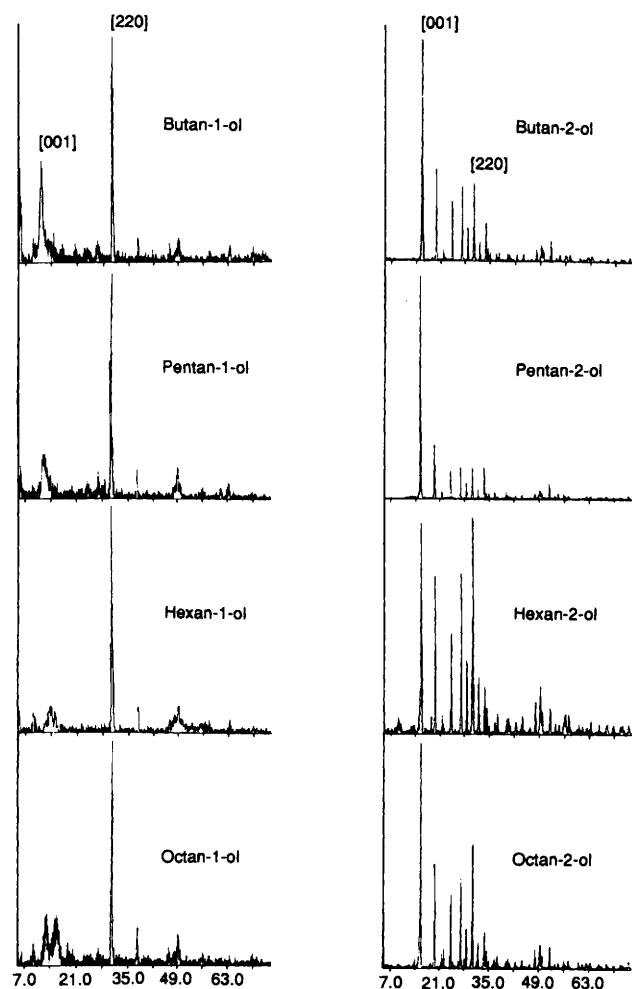


Fig. 1 X-ray powder diffraction patterns of the products from the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with 1- or 2-alcohols (all diffraction lines can be assigned to $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$)

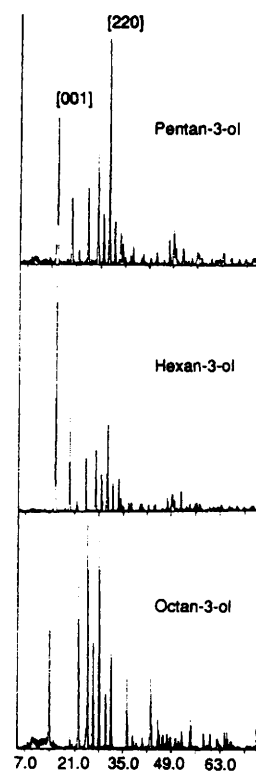


Fig. 2 X-ray powder diffraction patterns of the products from the reaction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with 3- alcohols. For pentan-3-ol and hexan-3-ol all diffraction lines can be assigned to $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. For octan-3-ol all diffraction lines can be assigned to $\text{VO}(\text{H}_2\text{PO}_4)_2$.

reflection is virtually the only feature of the diffraction pattern, whereas precursors prepared from 2-alcohols give $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ crystals for which the [001] reflection is the dominant feature of the diffraction pattern. This indicates that the two sets of alcohols are producing precursor crystals with distinctly different morphologies and this was confirmed by electron microscopy studies. A similar set of experiments was then carried out using 3-alcohols and the results are shown in Fig. 2. The C_5 and C_6 3-alcohols showed identical behaviour to the corresponding 2-alcohol, however, use of octan-3-ol as the reducing agent led to the exclusive formation of $\text{VO}(\text{H}_2\text{PO}_4)_2$ and in this case $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ was not observed. The formation of $\text{VO}(\text{H}_2\text{PO}_4)_2$ is observed only with octan-3-ol and this preparative method therefore provides a new simple route to this material. It is therefore clear from this study that using octan-1-ol, octan-2-ol or octan-3-ol as the reducing agent for $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ can lead to either $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ with controlled morphology or $\text{VO}(\text{H}_2\text{PO}_4)_2$ and this study provides the first simple demonstration of how control of precursor morphology can be achieved.

It is interesting to consider the origin of these structural effects. The differences in boiling point of the various alcohols is not considered to be important since the range of boiling points for each carbon number is relatively small. However, it is possible that the alcohols are incorporated in the structure of the precursor and so there may be a steric factor associated with the structure of the alcohol. Further evidence in support of this possibility is provided by a study of the thermal decomposition of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, prepared with butanol as solvent, in a thermal balance under vacuum together with evolved gas analysis by mass spectroscopy. This indicated that some of the alcohol is retained within the structure and this is very strongly bound since the alcohol decomposition products are only observed at a temperature higher than that required for the transformation of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ to $(\text{VO})_2\text{P}_2\text{O}_7$.

The conversion of the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor into the active catalyst phase, $(\text{VO})_2\text{P}_2\text{O}_7$, is known to occur via a topotactic transformation² when the precursor is heated with *n*-butane-air under reaction conditions (1.5% *n*-butane in air, GHSV = 1000 h^{-1} , 385 °C). One can expect that morpholog-

ical differences in the precursor will be translated into the final catalyst, and this is indeed observed. Precursors for which the [001] reflection is the main feature in the diffraction pattern lead to the formation of $(\text{VO})_2\text{P}_2\text{O}_7$ with lower surface areas (typically $ca 14 \text{ m}^2 \text{ g}^{-1}$) when compared to the final catalysts prepared from the precursors for which the [220] reflection is the main feature in the diffraction pattern, which give higher surface areas ($>40 \text{ m}^2 \text{ g}^{-1}$). Although the two catalysts have very similar specific activities ($ca 1.2 \times 10^{-5} \text{ mol maleic anhydride/m}^2\text{/h}$ for 1.5% *n*-butane in air, GHSV 1000 h^{-1} , 385 °C) indicating that the two catalysts have similar densities of active sites, the significantly higher surface area of the catalyst derived from the straight chain alcohol means that this material has the highest activity per mass of catalyst. This study therefore presents a simple but effective means of controlling the composition and morphology of vanadium phosphate precursors, and hence the final catalyst, that is based on the dehydration and reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

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