



Preparation of vanadium phosphate catalyst precursors for the selective oxidation of butane using α,ω -alkanediols

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ABSTRACT

Vanadium phosphate catalyst precursors were prepared from V_2O_5 and H_3PO_4 or $VOPO_4 \cdot 2H_2O$ using α,ω -alkanediols (1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol) as both the reducing agent and the solvent. A series of layered $VOHPO_4 \cdot HO(CH_2)_nOH$ ($n = 4-6$) materials intercalated with α,ω -alkanediols were obtained. The performance for butane oxidation of the final catalysts formed *via* the *in situ* transformation of the $VOHPO_4 \cdot HO(CH_2)_nOH$ precursors under reaction conditions is described. The final catalysts derived from the alkanediol intercalated materials were found to exhibit relatively low selectivities to maleic anhydride and comprised of V^V ($VOPO_4$) phases with an amorphous V^{IV} phase. However, when a crystalline ($V^{IV}O$) $_2P_2O_7$ phase is present, with small amounts of V^V phases, as with materials prepared with 1,4-butanediol, the specific and intrinsic catalytic activity are higher.

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1. Introduction

Vanadium phosphates are important industrial catalysts that are used for the selective oxidation of butane to maleic anhydride [1,2]. Vanadium pyrophosphate, $(VO)_2P_2O_7$, is thought to be the active phase for butane oxidation and this is typically prepared by calcination of the precursor, $VOHPO_4 \cdot 0.5H_2O$ [3–5], although there is evidence which indicates that the surface of these catalysts is amorphous [6–9]. The morphology of the precursor is maintained in the final catalyst as the transformation is topotactic. Therefore, the preparation of $VOHPO_4 \cdot 0.5H_2O$ materials with high surface areas and different morphologies are of interest. The main strategy for the synthesis of $VOHPO_4 \cdot 0.5H_2O$ involves the reduction of $VOPO_4 \cdot 2H_2O$ or a mixture of V_2O_5 and H_3PO_4 with an alcohol. The nature of the alcohol can have a large influence on the morphology [10] and the mechanism for the precursor formation has been studied [11,12].

Vanadium phosphates intercalated with alcohols [13] and amides [14] have been studied as novel layered materials. The intercalation of α,ω -alkanediols into $VOPO_4 \cdot 2H_2O$ has been studied previously by Beneš et al. [15]. Since each α,ω -alkane diol molecule has two hydroxyl groups at the terminal position of the alkane

chain, they show very different properties from alcohols when intercalated into $VOPO_4 \cdot 2H_2O$. Previously, attempts to modify the morphology of $VOHPO_4 \cdot 0.5H_2O$ with various α,ω -alkanediols used isobutanol as a co-solvent [16,17]. Taufiq-Yap and co-workers [18,19] reported the use of ethylene glycol as a reducing agent, resulting in an improved surface area. Following this reduction step, refluxing with distilled water decreased the crystallite size of the $VOHPO_4 \cdot 0.5H_2O$ precursor. The selective oxidation of butane was reported to improve when compared to standard materials, which was proposed to be related to the mobility and availability of lattice oxygen species. The preparation of intercalated vanadium hydrogen phosphates with longer chain α,ω -alkanediols in the absence of a co-solvent has not, to our knowledge, been reported. In this paper we report the preparation of $VOHPO_4 \cdot HO(CH_2)_nOH$ materials *via* the reduction of $VOPO_4 \cdot 2H_2O$, or directly from V_2O_5 and H_3PO_4 , using α,ω -alkanediols with varying chain length and investigate these as catalysts for selective butane oxidation.

2. Experimental

2.1. Preparation of $VOPO_4 \cdot 2H_2O$

Vanadium phosphate dihydrate ($VOPO_4 \cdot 2H_2O$) was prepared according to the literature [20]. V_2O_5 (2.5 g) was refluxed with H_3PO_4 (85%, 15.0 ml, Aldrich) in water (60 ml) for 16 h. The yellow

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Table 1
Preparation conditions of the catalyst precursors.

Precursor	Method ^a	Solvent/reductant
VPDI	VPD	Isobutanol
VPD4	VPD	1,4-Butanediol
VPD5	VPD	1,5-Pentanediol
VPD6	VPD	1,6-Hexanediol
VPO4	VPO	1,4-Butanediol
VPO5	VPO	1,5-Pentanediol
VPO6	VPO	1,6-Hexanediol

^a VPO = $V_2O_5 + H_3PO_4$ refluxed with solvent/reducing agent, VPD = $VOPO_4 \cdot 2H_2O$ refluxed with solvent/reducing agent.

solid was recovered by filtration, washed with acetone and then dried in air (110 °C, 16 h).

2.2. Preparation of $VOHPO_4 \cdot HO(CH_2)_nOH$

$VOHPO_4 \cdot HO(CH_2)_nOH$ was synthesized by two routes, described as the VPO and VPD methods [21]. The VPO method denotes the reduction of V_2O_5 in the presence of H_3PO_4 in organic media. In a typical experiment, V_2O_5 (2.5 g) and H_3PO_4 (3.49 g, aqueous 85 vol%, P:V = 1:1) were reacted for 16 h at 125 °C with stirring. The resultant blue solid was recovered by vacuum filtration, washed with acetone and dried (110 °C, 16 h). The VPD method involves the reduction of vanadium phosphate dihydrate, $VOPO_4 \cdot 2H_2O$, with an alcohol. In a typical experiment, $VOPO_4 \cdot 2H_2O$ (1.0 g) was reacted with α, ω -alkanediol (50:1 alcohol:V molar ratio) for 16 h at 125 °C. The resultant blue solid was recovered by vacuum filtration, washed with acetone and dried in air (110 °C, 8 h). The designations and preparation conditions for the different vanadium phosphate precursors are listed in Table 1.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Panalytical X'pert Pro diffractometer using Ni filtered $CuK\alpha$ radiation (operating at 40 kV, 40 mA). Scans were in the range 10–80° 2θ . All patterns were indexed using the ICDD database (International Centre for Diffraction Data, Pennsylvania, USA). Raman spectra were obtained using a Renishaw inVia Raman Microscope fitted with a green Ar^+ laser ($\lambda = 514.532$ nm). Scanning electron microscopy (SEM) was performed using a Hitachi 326YO-N instrument. BET surface area measurements by nitrogen adsorption were carried out at –196 °C using a Micromeritics ASAP 2000 instrument.

2.4. Catalytic evaluation for butane oxidation

A micro-reactor was used to carry out catalyst testing for the oxidation of butane. A feedstock composition of 1.7% butane in air was fed at a rate of 10 ml min^{-1} into a stainless-steel tube reactor typically containing 0.20 g of precursor held in place by plugs of quartz wool. The reactor was heated to the reaction temperature at a ramp rate of 3 °C min^{-1} . Product analysis was by on-line GC (Varian 3800). Carbon balances obtained were typically 95–105%. Precursors were activated *in situ* at 400 °C for >72 h.

3. Results and discussion

3.1. Catalyst precursor characterization

A standard vanadium phosphate precursor, $VOHPO_4 \cdot 0.5H_2O$ (VPDI), was synthesized *via* the VPD method with isobutanol. The d spacing of the (001) reflection (hereafter denoted $d_{(001)}$) was determined to be 0.57 nm from the XRD pattern (Fig. 1a) and SEM analysis (Fig. 1b) confirmed that the material had a rosette structure with a particle size of 1–5 μm . The position of the (001) reflection is an indication of the interlayer spacing between the vanadium phosphate layers and so can be used to determine whether intercalation of the alcohols has occurred.

The low angle XRD patterns of the precursors produced *via* the VPD method with α, ω -alkanediols are shown in Fig. 2. The $d_{(001)}$ spacing was found to increase to 1.09 and 1.21 nm when the solvent used was 1,4-butanediol or 1,5-propanediol respectively. The multiple reflections observed at the (001) position in the pattern of VPD6 (Fig. 2) suggest that intercalated 1,6-hexanediol could adopt different conformations with different interlayer spacings. This has been observed previously for $VOPO_4 \cdot 2H_2O$ intercalated with benzyl alcohol [22]. These results indicate that a series of α, ω -alkanediol intercalated compounds with the general formula, $VOHPO_4 \cdot HO(CH_2)_nOH$, had been formed. This demonstrates that α, ω -alkanediols have more affinity to the vanadium phosphate layers than mono-functionalised alcohols which typically form $VOHPO_4 \cdot 0.5H_2O$ even though the alcohol is in excess (V:alcohol molar ratio = 1:50) [21]. The stoichiometry of the intercalated material formed is based on thermal analysis performed by Beneš et al. [15] which was found to be 1:1 with respect to $VOHPO_4 \cdot HO(CH_2)_nOH$ compounds were also synthesized *via* the VPO method using the α, ω -alkanediols. The increasing shift of the (001) reflection with increasing carbon number of the alkanediol is similar to the trend found for the materials prepared *via* the VPD route (Fig. 3). The relationship between the carbon chain length of

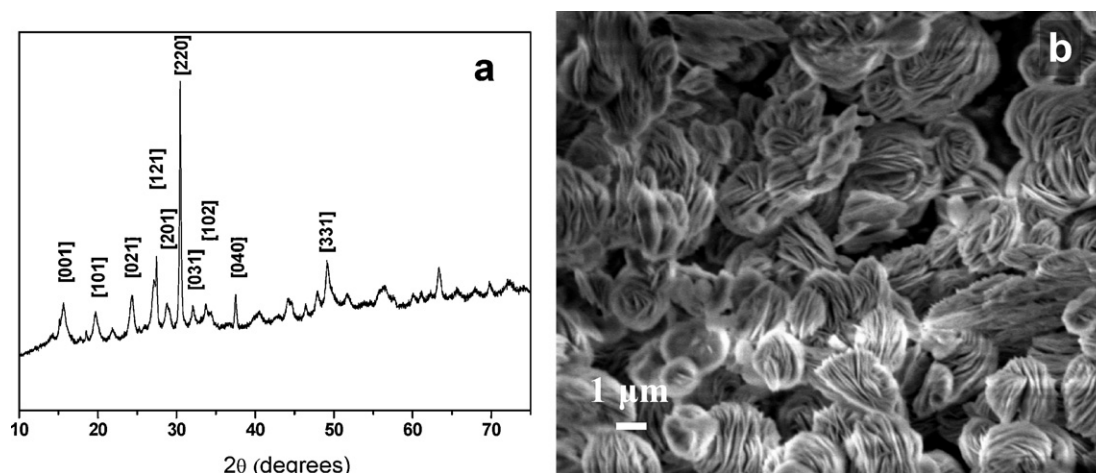


Fig. 1. (a) XRD pattern and (b) SEM image of the standard $VOHPO_4 \cdot 0.5H_2O$ precursor VPDI.

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