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Investigation of Vanadyl Pyrophosphate Catalysts Synthesised from Three Different Routes

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Three different methods were used to prepare vanadyl pyrophosphate catalysts: (i) VPO, which is the classical organic way of preparing vanadyl pyrophosphate by reacting V_2O_5 in a mixture of isobutanol and benzyl alcohol prior to the addition of H_3PO_4; (ii) VPA, the earliest way of preparation by digesting V_2O_5 in concentrated HCl prior to H_3PO_4 addition, and (iii) VPD, the latest way of preparation by preparing $VOPO_4{\cdot}2H_2O$ before reacting with isobutanol. The precursors were then calcined in *n*-butane/air (0.75% *n*-butane/air) for 75 h at 673 K. The catalysts obtained were characterised by BET surface area measurements, ICP, XRD, volumetric titration and SEM-EDAX.

Key Words: Vanadyl pyrophosphate catalysts, *n*-Butane partial oxidation, Maleic anhydride, BET, ICP, XRD, SEM-EDAX

INTRODUCTION

Vanadyl pyrophosphate has long been recognised as the selective catalyst for partial oxidation of *n*-butane to maleic anhydride. It catalysed the only commercially viable alkane oxidation and has been used extensively since mid 1960's[1]. As the transformation of the precursor to the final catalyst is topotactic[2, 3], hence the final catalyst morphology can be readily controlled at the precursor stage[4]. Thus, a lot of efforts on this catalyst system have been concentrated on the preparation of the precursor[5–8].

The earliest method of preparation was by hydrochloric acid digestion of a vanadium source prior to phosphorus source addition, which is more fondly known as the 'aqueous method'[9, 10] and denoted throughout this paper as VPA. The presence of traces of chloride presents engineering difficulty, as it is corrosive to reactors[11]. Due to this major disadvantage, a better method has been developed which substitutes both acid and water needed in the aqueous method with organic solvents. This method is known as the 'organic method' (VPO)[12] and the commonly used solvents are a mixture of benzyl alcohol and isobutanol. Both of the above methods generate the precursor, which is vanadium hydrogen phosphate hemihydrate, $VOHPO_4{\cdot}1/2H_2O$. This precursor would transform topotactically to the active vanadyl pyrophosphate, $(VO)_2P_2O_7$ catalysts after calcination in reaction conditions[2].

A number of new methods have been suggested by researchers worldwide in the preparation of precursors, which produced better catalysts in terms of selectivity and activity. One of the methods is through a route based on alcohol reduction of $VOPO_4 2H_2O$. This route involves the generation of $VOPO_4 \cdot 2H_2O$ and further reduction to $VOHPO_4 \cdot \frac{1}{2}H_2O$[9, 10]. The precursor obtained this way is claimed to lead to the identification of a high area preparation method of the catalyst[4].

As such, the purpose of this paper is to investigate the properties of the vanadium phosphorus oxide catalysts synthesised by three different routes using BET surface area measurements, ICP, XRD, volumetric titration and SEM-EDAX.

EXPERIMENTAL

Preparation of Vanadyl Pyrophosphate Catalysts

(a) Via organic route (VPO): Vanadium pentoxide, V_2O_5 (15.0 g from Fisher) was suspended by rapid stirring into a mixture of isobutyl alcohol (90 mL from BDH) and benzyl alcohol (60 mL from BDH). The vanadium oxide-alcohol mixture was refluxed for 3 h at 393 K with continuous stirring. The mixture was then cooled to room temperature and left stirring at this temperature overnight. Ortho-phosphoric acid (85% from Fisher) was added in such a quantity as to obtain the desired P : V (*ca.* 1 : 1) atomic ratio. The resulting solution was then heated again to 393 K and maintained under reflux with constant stirring for 2 h. The slurry was then filtered, washed and dried at 423 K overnight to obtain the precursor vanadyl hydrogen phosphate hemihydrated, $VOHPO_4 \cdot \frac{1}{2}H_2O$ denoted VPOP.

(b) via $VOPO_4 \cdot 2H_2O$ phase (VPD): The preparation involved a two-step procedure with $VOPO_4 \cdot 2H_2O$ as an intermediate before obtaining the precursor $VOHPO_4 \cdot \frac{1}{2}H_2O$. $VOPO_4 \cdot 2H_2O$ was prepared by reacting V_2O_5 (10.0 g from Fisher) with H_3PO_4 (60 mL, 85% from Fisher) in water (240 mL) under reflux with continuous stirring for 24 h. The yellow solid was recovered by filtration, washed sparingly with water and oven dried at 385 K for 16 h. $VOPO_4 \cdot 2H_2O$ was then refluxed with isobutanol (1 g/20 mL) for 21 h and the solid product was recovered by filtration and dried in air at 385 K for 16 h to obtain the precursor $VOHPO_4 \cdot \frac{1}{2}H_2O$, denoted VPDP.

(c) via aqueous route (VPA): Vanadium pentoxide, V_2O_5 (15.0 g from Fisher) was refluxed together with concentrated HCl (37%, 200 mL) at 393 K with continuous stirring for 1.5 h, at which time the solution was dark blue in colour. Ortho-phosphoric acid (85% from Fisher) was added in such a quantity as to obtain the desired P : V atomic ratio. The resulting solution was then heated again to 393 K and maintained under reflux with constant stirring for a further 1.5 h. The solution was then evaporated to near dryness to a blue-green paste, which was dried in air at 385 K for 16 h. The resulting green-blue solid was refluxed for 2 h with distilled water (1 g/20 mL). The suspension was then filtered hot and dried in air at 385 K for 16 h to give a blue solid, which was the precursor, denoted VPAP.

Calcination of precursors: All of the precursors obtained were calcined in reaction flow of *n*-butane/air mixture for 75 h at 673 K. The final catalysts prepared by organic, dihydrate and aqueous methods were denoted VPO75, VPD75 and VPA75, respectively.

Catatysts Characterisation: The BET (Brunauer-Emmer-Teller) surface area and the porosity of the catalysts were measured by using nitrogen adsorption at 77 K. This was done using a micromeritics ASAP 2000.

The bulk chemical composition was determined by using a sequential scanning inductively coupled plasma-atomic emission spectrometer (ICP-AES) Perkin-Elmer Emission Spectrometer model Plasma 1000. Each sample was digested by concentrated nitric acid (10 M) with slow heating. The resulting solution was diluted with distilled water to 1000 mL.

The bulk average valency of vanadium was determined by volumetric titration of each catalyst, which had been dissolved in sulphuric acid (2 M). Firstly, potassium permanganate solution (0.01 M) was used to oxidise V^{3+} and V^{4+} to V^{5+} followed by reduction by ammonium iron(II) sulfate solution (0.01 M) with diphenylamine as redox indicator. Secondly, the solution was titrated by ammonium iron(II) sulphate solution (0.01 M) with diphenylamine as redox indicator to determine V^{5+} content.

X-ray diffraction (XRD) analyses were carried out using a Shimadzu diffractometer model XRD-6000 diffractometer employing CuK_α radiation generated by a Phillips glass diffraction X-ray tube broad focus 2.7 kW type on the catalysts at ambient temperature. SEM was done using a Jeol JSM-6400 electron microscope coupled with EDAX extension provided by Oxford Instrument. The samples were coated with gold by a sputter coater. The photographs were captured using a Mamiya camera with Kodak Verichrome Pan 100 black and white negatives.

RESULTS AND DISCUSSION

BET surface area measurement and porosity: The specific surface area for VPD75, VPO75 and VPA75 are 14.5, 18.2 and 4.4 $m^2\ g^{-1}$, respectively. The surface areas for VPA75 and VPO75 are comparable to Hutching *et al.*[4, 13] which they reported to be 4 and 14 $m^2\ g^{-1}$, respectively. However, surface area for VPD75 in our study is only a third of the value reported by the same group. This variation could be attributed to the use of higher *n*-butane concentration (1.75% *n*-butane/air) used in calcinations by which only VPD might have been affected. The adsorption isotherms encountered are of Type II in the classification as shown in Fig. 1, indicating the presence of mesopores. The type of loop observed is Type H3 indicating the material is constituted of aggregates of plate-like particles giving rise to slit-shape pores[14].

Chemical Analysis

(a) Chemical compositions: Chemical analysis using ICP indicated that the respective bulk P/V ratio for VPD75, VPO75 and VPA75 are 1.03, 1.04 and 1.14. These values are in the intended optimal P/V ratio range of 1.0–1.2.

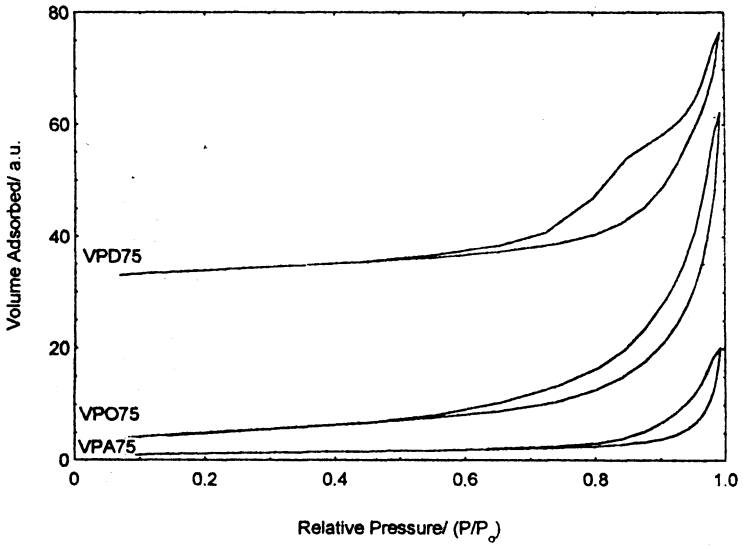

Fig. 1. Isotherm plot for VPD75, VPO75 and VPA75 catalysts.

(b) Oxidation state of vanadium: The bulk average oxidation states of these three catalysts were determined using volumetric titration and the values were calculated by solving the equations below[15]:

$$(2V^{3+} + V^{4+})(V_c) = [MnO_4^-](V_a)$$

$$(V^{3+} + V^{4+} + V^{5+})(V_c) = [Fe^{2+}](V_b)$$

$$(V^{5+})(V_c) = [Fe^{2+}](V_b)$$

where V^{3+}, V^{4+} and V^{5+} are the oxidation states of vanadium, $[MnO_4]$ is the concentration of potassium permanganate solution, $[Fe^{2+}]$ is the concentration of ammonium iron(II) sulphate solution, V_a is the volume af potassium permanganate solution used, V_b is the volume of ammonium iron(II) sulphate solution used and V_c is the volume of the respective catalyst solution used. The average oxidation states obtained are 4.23, 4.15 and 4.56 for VPD75, VPO75 and VPA75, respectively. The result shows that the aqueous method gave the highest average oxidation state.

The specific surface area of the catalysts, their respective P/V ratio, the bulk average oxidation state as well as the breakdown of V^{4+} and V^{5+} composition are summarised in Table 1.

X-Ray diffraction: XRD patterns of the precursors prepared through these three different routes show remarkable resemblance. All of the precursors showed characteristic peaks that matched perfectly with $VOHPO_4{\cdot}0.5H_2O$ (JCPDS File No. 37–0269). The peaks at $2\theta = 15.6°, 27.0°$ and $30.4°$ correspond to (001), (121) and (220), respectively as shown in Fig. 2. The aqueous method gave the highest crystallinity compared to the other two methods. Fig. 3 shows diffractogram of

TABLE-1
SPECIFIC SURFACE AREA MEASUREMENTS AND CHEMICAL ANALYSES FOR VPO75, VPA75 AND VPD75

Catalysts	Specific surface area (m^2g^{-1})	P/V atomic ratio	Average oxidation state of vanadium	V^{4+} (%)	V^{5+} (%)
VPD75	14.5	1.03	4.23	77	23
VPO75	18.2	1.04	4.15	85	15
VPA75	4.4	1.14	4.56	44	56

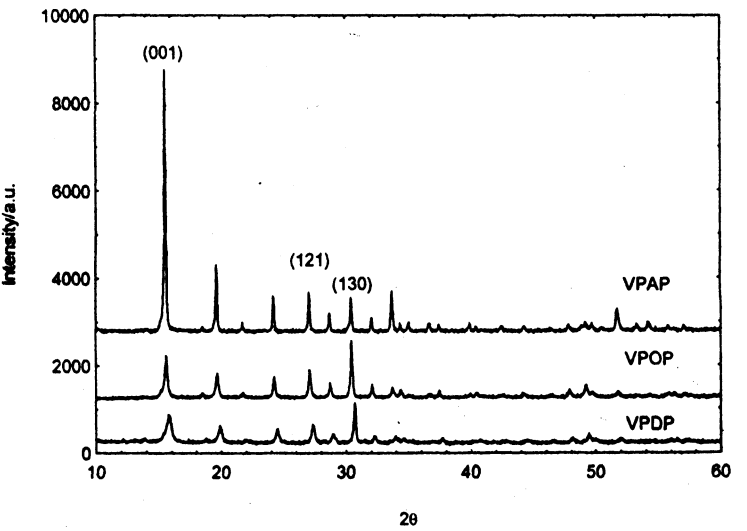

Fig. 2. XRD patterns of precursors VPDP, VPOP and VPAP.

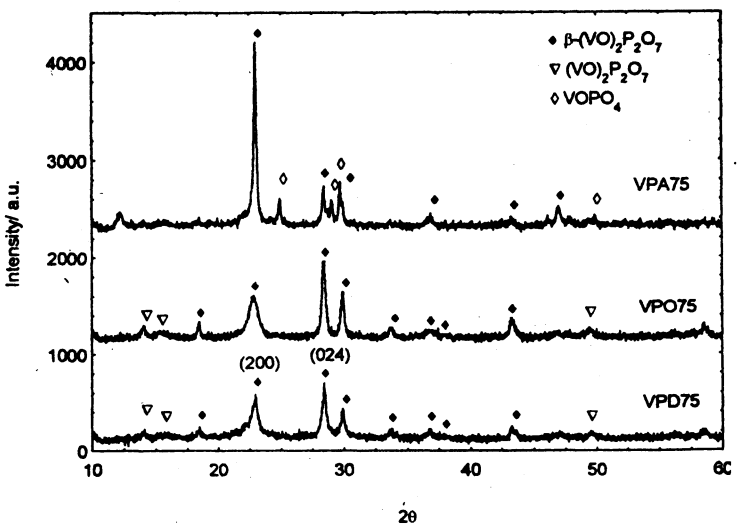

Fig. 3. XRD patterns of VPD75, VPO75 and VPA75 catalysts.

the catalysts having calcined in n-butane/air mixture for 75 h. VPD75 and VPO75 show characteristic peaks that matched perfectly with vanadyl pyrophosphate with good crystallinity. Both catalysts consist of $(VO)_2P_2O_7$ (JCPDS File No. 34-1381) and β-$(VO)_2P_2O_7$ (JCPDS File No. 41-0698), with the latter being the majority component. The existence of V^{5+} phase indicated by volumetric titration was not detected by XRD probably due to its low concentration (23% and 15% for VPD75 and VPO75, respectively). In contrast, VPA75 consists of a mixture of $(VO)_2P_2O_7$ and a V^{5+} phase, *i.e.*, $VOPO_4$ (JCPDS File No. 34-1247) which were observed at 24.92°, 29.06°, 29.72° and 49.92°. This is in agreement with volumetric titration results which gave the average oxidation state of 4.56 with concentration of V^{5+} at 55%. VPA75 also shows an outstanding development of diffraction peak at $2\theta = 22.98°$, which corresponds to development of (200) plane. This shows that while deriving from the same precursor, difference in preparation method had led to formation of final catalysts with different crystal phase.

Particle thickness of the (200) and (024) planes, which are crucially involved in the reaction, can be calculated theoretically using Debye-Scherrer equation:

$$t = \frac{0.9\lambda}{\beta_{hkl} \cos \theta_{hkl}}$$

where t is the particle thickness for (hkl) phase, λ is the X-ray wavelength of radiation for CuK_α, β_{hkl} is the full-width at half maximum (FWHM) at (hkl) peak in radian and θ_{hkl} is the diffraction angle for (hkl) phase[16]. The particle thicknesses for VPD75 at (200) and (024) were, as such, calculated to be 122.4 Å and 174.1 Å, respectively, while for VPO75 these values are 98.8 Å and 237.4 Å respectively. VPA75 gave higher values at 347.8 Å and 329.5 Å, respectively.

TABLE-2
XRD DATA FOR VPO75, VPA75 AND VPD75

Catalysts	I_{200}/I_{024}	$FWHM_{200}$	$FWHM_{024}$	t_{200} (Å)	t_{024} (Å)
VPD75	0.83	0.6617	0.2486	122.44	174.14
VPO75	0.49	0.8200	0.3450	98.79	237.43
VPA75	4.76	0.2330	0.4704	347.78	329.50

Scanning Electron Microscope (SEM): The final catalysts show different and distinct morphology with each other as in Fig. 4–6, VPD75 shows spheres resembling a rosebud with variable sizes but a uniform shape. These $(VO)_2P_2O_7$ agglomerates are the dominant structure that preferentially exposes the (100) crystal plane as had been stated by Hutchings *et al.*[4] The existence of α_{II}-$VOPO_4$ (a V^{5+} species) with the (001) plane preferentially exposed and the unreacted $VOHPO_4 \cdot \frac{1}{2}H_2O$ could not be verified, however, as had been claimed by Hutchings *et al.*[4], even though chemical analysis had shown the presence of some V^{5+} species.

Fig. 4. SEM micrograph for VPD75

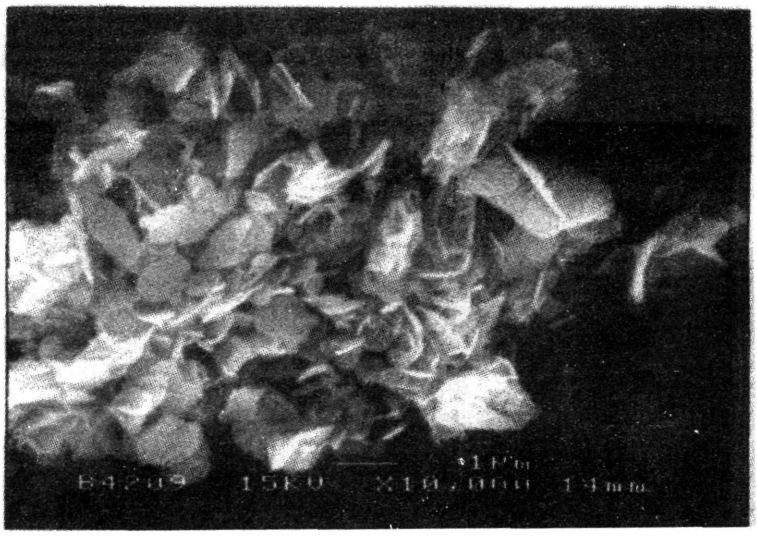

Fig. 5. SEM micrograph for VPO75

VPO75, on the other hand, appeared to have a more disorganized structure showing very thin oblong platelets closely packed together forming rosette-shaped agglomerates. These are the $(VO)_2P_2O_7$ agglomerates that preferentially expose the (100), (021) and (012) faces.

VPA75, instead of forming agglomerates like VPD75 or VPO75, shows a simpler shape of larger and uniform platelets. These platelets are assigned to the α_{II}-$VOPO_4$ crystallites. The dominance of these V^{5+} species is reflected by the

high V^{5+} concentration determined by chemical analysis. There are, of course, crystallites of V^{4+} species present as well which resembled more to those in VPO75 than in VPD75.

Fig. 6. SEM micrograph for VPA75

The formation of more and smaller platelets in VPO75 explains the fact that its surface area is the highest compared to the larger and uniform platelets formed in VPA75, which has the smallest specific surface area of all with VPD75 in between them.

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