

Synthesis and Physico-Chemical Investigation of Vanadium Phosphorus Oxide Catalysts Derived from $\text{VO}(\text{H}_2\text{PO}_4)_2$

Y. H. Taufiq-Yap & C. K. Goh

Department of Chemistry,
Faculty of Science and Environmental Studies,
Universiti Putra Malaysia, 43400 UPM, Serdang,
Selangor, Malaysia

Received: 13 June 2002

ABSTRAK

Mangkin vanadium fosforus oksida telah disediakan melalui $\text{VO}(\text{H}_2\text{PO}_4)_2$ dengan menggunakan dua kaedah: i) tindak balas V_2O_4 dengan $\sigma\text{-H}_3\text{PO}_4$ dan ii) penurunan $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ dengan menggunakan oktan-3-ol. Prekursor ini dikalsinkan dalam campuran *n*-butana/udara pada 673 K selama 75 jam. Mangkin ini dicirikan dengan menggunakan pelbagai teknik, seperti luas permukaan BET, XRD, FTIR dan SEM.

ABSTRACT

Vanadium phosphorus oxide catalysts were prepared via $\text{VO}(\text{H}_2\text{PO}_4)_2$ by using two methods: i) reaction of V_2O_4 with $\sigma\text{-H}_3\text{PO}_4$ and ii) reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with octan-3-ol. The precursors were calcined in *n*-butane/air mixture at 673 K for 75 h. These catalysts were characterised by using various techniques, such as BET surface area, XRD, FTIR and SEM.

Keywords: Vanadium phosphorus oxide, *n*-butane, maleic anhydride, vanadyl dihydrogen phosphate, partial oxidation

INTRODUCTION

Vanadium phosphorus oxide catalysts have been widely accepted to contain selective and active phase for heterogeneous oxidation of *n*-butane to maleic anhydride (Centi 1993). Vanadyl pyrophosphate, $(\text{VO})_2\text{P}_2\text{O}_7$ (V^{4+} phase with a P/V ratio of 1) was claimed to be the main crystalline phase for industrial catalysts. This phase is mostly generated from the precursor phase, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ via a topotactic transformation during the catalyst activation (Centi 1993; Johnson *et al.* 1984). Initially, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor can be prepared by: i) using aqueous HCl as the reducing agent for V_2O_5 and ii) using isobutanol as the reducing agent and solvent for V_2O_5 . Sananes *et al.* (1994; 1995a; 1995b; 1996) have investigated the preparation of VPO catalysts derived from $\text{VO}(\text{H}_2\text{PO}_4)_2$. They claimed that this catalyst displays ultraspecific formation of maleic anhydride and no CO or CO_2 formation at low *n*-butane conversion. However, Hannour *et al.* (1998) found that the activity and selectivity of the amorphous and partly crystalline $\text{VO}(\text{PO}_3)_2$ catalysts were not exceeding 40% with formation of CO and CO_2 . A small amount of furan, acrylic acid, acetic acid and acrolein were also observed. These findings are in agreement with

Wang *et al.* (2000) where maleic anhydride selectivity observed was typically 50% with CO and CO₂ formation. Later, Bartley *et al.* (2000a; 2000b) introduced the synthesis of catalyst derived from VO(H₂PO₄)₂ precursor by using aldehydes and ketones as reducing agents. They reported that the selectivity to maleic anhydride is typically 20-30% due to impurity of VO(H₂PO₄)₂. Even with these controversies in the literatures, continual efforts are still being made to investigate the physico-chemical properties of VO(H₂PO₄)₂ catalyst. In this study, vanadium phosphorus oxide catalysts derived from VO(H₂PO₄)₂ precursor were prepared using two methods: i) reaction between V₂O₅ with phosphoric acid and ii) reduction of VOPO₄·2H₂O by using 3-octanol. Their physico-chemical characteristics were compared to the catalyst prepared by the normal organic method via VOHPO₄·0.5H₂O precursor.

EXPERIMENT

Catalyst Preparation

Preparation of VOHPO₄·0.5H₂O

15 g of V₂O₅ (from Fluka) was suspended by rapid stirring into a mixture of isobutyl alcohol (90 mL) and benzyl alcohol (60 mL). The 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. The *o*-H₃PO₄ (85% from Merck) was added and further refluxed for 2 h. The blue slurry was then filtered, washed and dried at 373 K for 24 h. The resulting precursor is referred to as VPOpreA.

Preparation of VO(H₂PO₄)₂ from V₂O₅

10 g of V₂O₅ (from RdH) was refluxed with 82 mL of *o*-H₃PO₄ (85% from Merck) at 453 K for 1 h. The suspension was centrifuged and the solid was redispersed with diethyl ether. Finally, the product was dried at 373 K for 24 h. The resulting precursor is referred to as VPHpreA.

Preparation of VO(H₂PO₄)₂ from Reduction of VOPO₄·2H₂O by Using 3-octanol

VOPO₄·2H₂O was prepared by reacting V₂O₅ (12 g from Fluka) with *o*-H₃PO₄ (115.5 g, 85% from Merck) in water (24 mL H₂O/g solid) under reflux for 24 h. The yellow solid was recovered by filtration, washed with water and then acetone and dried at 383 K for 24 h. VOPO₄·2H₂O recovered was refluxed with 3-octanol (50 ml alcohol/ mol VOPO₄·2H₂O) for 21 h. Then, the blue solid product was obtained by filtration and was dried at 373 K for 24 h. The resulting precursor is referred to as VPHpreB.

All the precursors were calcined in *n*-butane/air mixture (0.75% *n*-butane in air) for 75 h at 673 K and the resulting catalysts were denoted as VPO, VPH-A and VPH-B, respectively.

Catalysts Characterisation

X-ray diffraction (XRD) analyses were carried out by 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.

Fourier transform infrared (FTIR) spectra were obtained by using a Perkin Elmer 1725X Spectrometer. The instrument was equipped with an infrared source element, a KBr beam splitter and a detector.

B.E.T. (Brunauer-Emmer-Teller) surface area measurements were carried out by using nitrogen adsorption-desorption at 77 K using a Micromeritics ASAP 2000 instrument.

SEM was done using a JOEL JSM-6400 electron microscope. The samples were coated with gold by using a Sputter Coater. The photographs were captured using a Mamiya camera with Kodak Verichrome Pan 100 black and white negatives.

RESULTS AND DISCUSSION

B.E.T. Surface Area Measurements

B.E.T. surface area of the two catalysts derived from $\text{VO}(\text{H}_2\text{PO}_4)_2$ precursor were significantly low, *i.e.* $1.1 \text{ m}^2\text{g}^{-1}$ for VPH-A and $2.3 \text{ m}^2\text{g}^{-1}$ for VPH-B compared to $18.2 \text{ m}^2\text{g}^{-1}$ for VPO catalyst. This result is in agreement with those reported earlier by Sananes *et al.* (1995a; 1996), Hannour *et al.* (1998) and Bartley *et al.* (2000a; 2000b). The adsorption-desorption isotherms of nitrogen at 77 K for all the catalysts were shown in *Fig. 1*. These catalysts gave isotherms of Type II with the presence of hysteresis loop (Sing *et al.* 1985), indicating the presence of a mixture of porosity and mesopores. The hysteresis loop is a type E, indicating the presence of pore with ink-bottle shape or by pores having varying widths.

X-ray Diffraction

Fig. 2 shows the XRD patterns of all the precursors. VPOpre gave the characteristic peaks of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ (JCPDS File No. 37-0269) at $2\theta = 15.0^\circ$, 27.0° and 30.5° correspond to (001), (121) and (220) planes, respectively. VPHpreA showed only sharp diffraction peaks for $\text{VO}(\text{H}_2\text{PO}_4)_2$ (JCPDS File No. 40-0038) at $2\theta = 14.0^\circ$, 28.2° and 31.6° correspond to (110), (220) and (130) planes, respectively. However, VPHpreB gave diffraction peaks of a mixture of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{VO}(\text{H}_2\text{PO}_4)_2$. The peaks' relative intensities for VPHpreB are lower compared to VPOpre and VPHpreA.

The XRD patterns of VPO, VPH-A and VPH-B catalysts are shown in *Fig. 3*. VPO shows characteristic peaks of $(\text{VO})_2\text{P}_2\text{O}_7$ (JCPDS File No. 34-1381) with main peaks at $2\theta = 23.0^\circ$, 28.5° and 30.0° , which correspond to the reflections from (020), (204) and (221) planes, respectively. The diffractogram of VPH-A catalyst gave a poor crystalline of $\text{VO}(\text{PO}_3)_2$ in agreement with the finding by Hannour *et al.* (1998) with a very broad peak spanning $2\theta = 10.0^\circ - 60.0^\circ$,

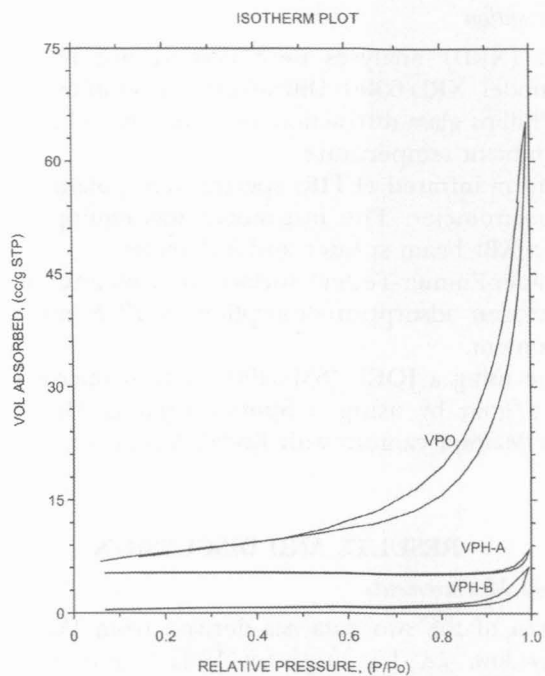


Fig. 1: The adsorption-desorption isotherms of nitrogen at 77 K for VPO, VPH-A and VPH-B catalysts

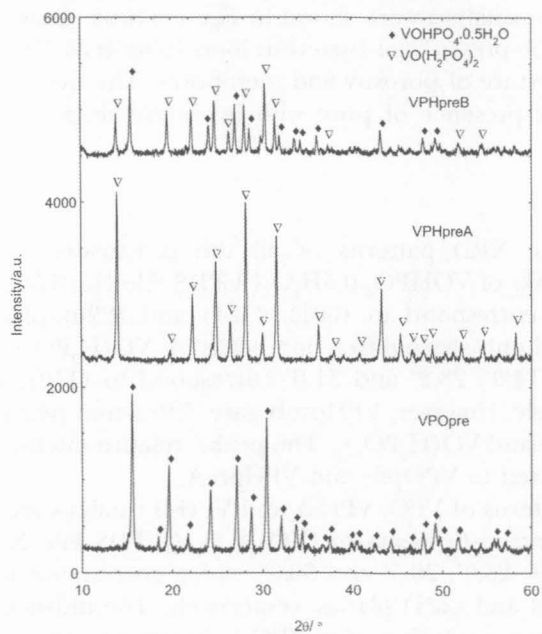


Fig. 2: XRD patterns of VPOpre, VPHpreA and VPHpreB

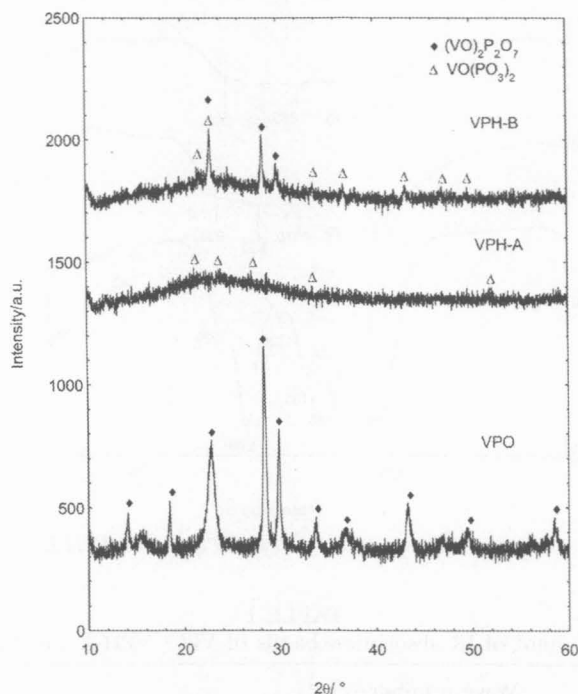


Fig. 3: XRD pattern of VPO, VPH-A and VPH-B

indicating the presence of an amorphous phase. However, small peaks at $2\theta = 22.3^\circ, 24.0^\circ, 27.0^\circ, 32.8^\circ$ and 53.0° were observed which correspond to (001), (220), (211), (040) and (260) planes, respectively and assigned to $\text{VO}(\text{PO}_3)_2$ (JCPDS File No. 34-1433). The XRD patterns of VPH-B catalyst gave $(\text{VO})_2\text{P}_2\text{O}_7$ as the main phase at $2\theta = 22.9^\circ, 29.0^\circ$ and 30.0° . Additional smaller peaks which were also observed could all be assigned to $\text{VO}(\text{PO}_3)_2$.

Fourier Transform Infrared (FTIR)

FTIR spectra for VPO, VPH-A and VPH-B catalysts were shown in Fig. 4. VPO shows the absorption bands at 1248, 1148, 1100, 1030, 970, 930, 740 cm^{-1} and a series of bands in the region below 700 cm^{-1} . However, VPH-A and VPH-B revealed a broad band in the region 1230-900 cm^{-1} . The bands with wave numbers above 700 cm^{-1} can be assigned to valence vibrations of P-O bonds in various anions of phosphorus with oxygen and the bands from the region below 700 cm^{-1} can be assigned to deformation vibration of these groupings (Brutovsky *et al.* 1982). The absorption bands at 1248, 1148, 1100 and 1030 cm^{-1} of VPO are assigned to vibration of two PO_3 groups, which differ by the type of symmetry, and the bands at 970, 930 and 740 cm^{-1} can be assigned to the vibrations $\text{V}=\text{O}$, $\nu_{\text{as}}(\text{POP})$ and $\nu_{\text{s}}(\text{POP})$, respectively. The band at 1230 cm^{-1} for VPH-A and VPH-B can be assigned to $\nu_{\text{as}}(\text{PO}_3)$. Detailed assignment of the observed bands is shown in Table 1.

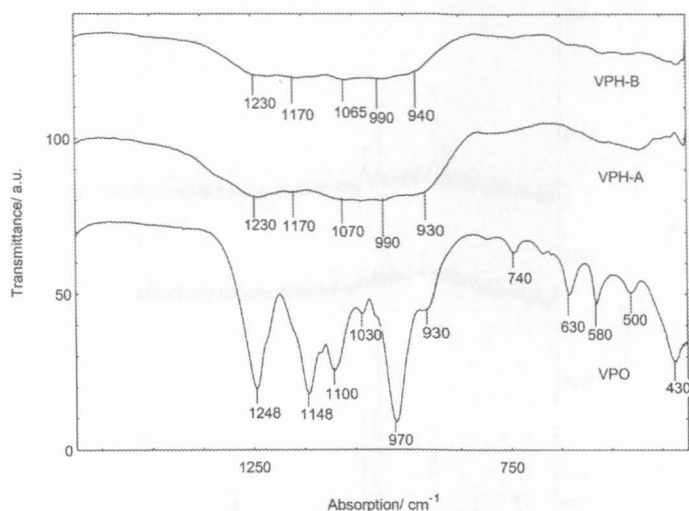


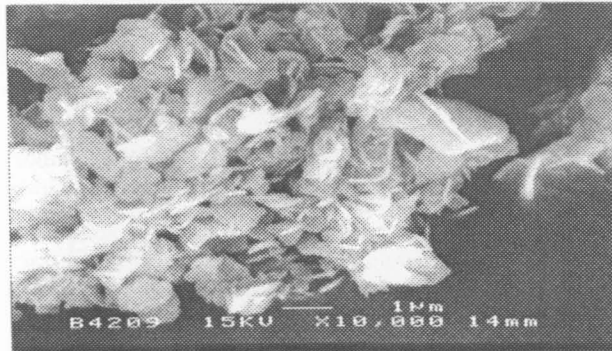
Fig. 4: FTIR spectrum of VPO, VPH-A and VPH-B

TABLE 1
Assignment of IR absorption bands of VPO, VPH-A and VPH-B

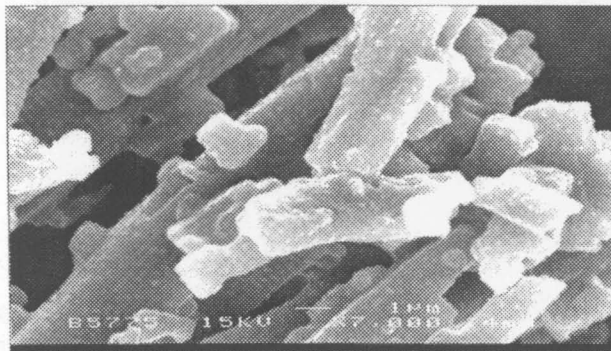
Wave number (cm ⁻¹)			Vibration
VPO	VPH-A	VPH-B	
1248	1230	1230	$\nu_{as}(\text{PO}_3)$
1148, 1100, 1030	1170, 1050, 1036	1140, 1065	$\nu_s(\text{PO}_3)$
970	990	990	V=O
930	940	-	$\nu_{as}(\text{POP})$
740	-	-	$\nu_s(\text{POP})$

Scanning Microscopy Electron

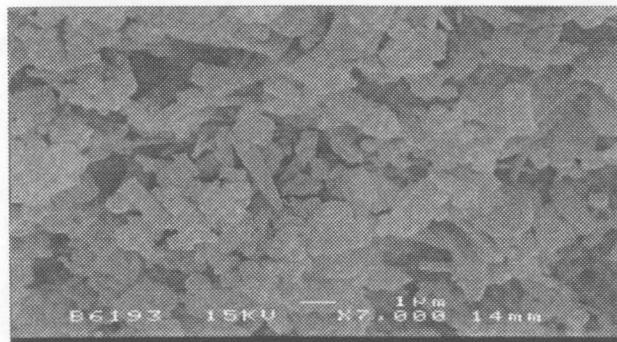
The SEM micrographs for VPO, VPH-A and VPH-B catalysts shown in Fig. 5 gave distinctly different morphologies. VPO catalyst appeared to be rosette-shape agglomerate, consisting of plate-like crystals which was similar to the reported morphology for $(\text{VO})_2\text{P}_2\text{O}_7$ catalyst (Kiely *et al.* 1995). The dominant morphology observed for VPH-A was blocky-shape with regular sided oblong crystallites with the ratio of the sides being 1:1:4 regardless of the dimensions of the crystal. This result is in agreement with the findings reported for $\text{VO}(\text{PO}_3)_2$ obtained by Sananes *et al.* (1996). The VPH-B consists of a mixture of smaller oblong blocky-shape and plate-like crystallites with the size of 1-3 μm in length and less than 100 nm in thickness. This result is consistent with the XRD result where the particle thickness at (040) for VPH-B and VPH-A catalysts are 921.6 and 2072.0 \AA , respectively.



(a)



(b)



(c)

Fig. 5: SEM micrographs of (a) VPO, (b) VPH-A and (c) VPH-B

ACKNOWLEDGEMENT

Financial assistance from the Malaysian Ministry of Science, Technology and Environment is gratefully acknowledged.

REFERENCES

- BARTLEY, J. K., C. RHODES, C. J. KIELY, A. F. CARLEY and G. J. HUTCHINGS. 2000. *n*-Butane oxidation using $\text{VO}(\text{H}_2\text{PO}_4)_2$ as catalyst derived from an aldehyde/ketone based preparation method. *Phys. Chem. Chem. Phys.* **2**: 4999-5006.
- BARTLEY, J. K., R. P. K. WELLS and G. J. HUTCHINGS. 2000. The unexpected role of aldehydes and ketones in the standard preparation method for vanadium phosphate catalysts. *J. Catal.* **195**: 423-427.
- BRUTOVSKY, M., S. GEREJ, F. VASILCO and J. GEREJOVA. 1982. X-ray diffractograms and IR spectra of modified vanadium-phosphate catalysts. *Col. Chec. Chem. Commun.* **47**: 1290-1300.
- CENTI, G. 1993. Vanadyl pyrophosphate catalysts. *Catal. Today* **16**: 5.
- HANNOUR, F. K., A. MARTIN, B. KUBIAS, B. LUCKE, E. BORDES and P. COURTINE. 1998. Vanadium phosphorus oxides with P/V=2 used as oxidation and ammoxidation catalysts. *Catal. Today* **40**: 263-272.
- JOHNSON, J. W., D. C. JOHNSTON, A. J. JACOBSON and J. F. BRODY. 1984. Preparation and characterization of $\text{VO}(\text{HPO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ and its topotactic transformation to $(\text{VO})_2\text{P}_2\text{O}_7$. *J. Am. Chem. Soc.* **106**: 8123-8128.
- KIELY, C. J., S. SAJIP, I. J. ELLISON, M. T. SANANES, G. J. HUTCHINGS and J. C. VOLTA. 1995. Electron microscopy studies of vanadium phosphorus oxide catalysts derived from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. *Catal. Lett.* **33**: 357-368.
- SANANES, M. T., I. J. ELLISON, T. MARIA, J. C. VOLTA and G. J. HUTCHINGS. 1994. Control of the composition and morphology of vanadium phosphate catalyst precursors from alcohol treatment of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. *J. Chem. Soc. Chem. Commun.* **1**: 1039-1094.
- SANANES, M. T., G. J. HUTCHINGS and J. C. VOLTA. 1995. On the role of the $\text{VO}(\text{H}_2\text{PO}_4)_2$ precursor for *n*-Butane oxidation into maleic anhydride. *J. Catal.* **154**: 253-260.
- SANANES, M. T., G. J. HUTCHINGS and J. C. VOLTA. 1995. *n*-Butane to maleic anhydride and furan with no carbon oxide formation using a catalysts from $\text{VO}(\text{H}_2\text{PO}_4)_2$. *J. Chem. Soc. Chem. Commun.* **1**: 243-244.
- SANANES, M. T., I. J. ELLISON, S. SAJIP, A. BURROWS, C. J. KIELY, J. C. VOLTA and G. J. HUTCHINGS. 1996. *n*-Butane oxidation using catalysts prepared by treatment of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with octanol. *J. Chem. Soc. Faraday Trans.* **92**: 137-142.
- SING, K. S. W., D. H. EVERETT, R. A. W. HAUL, L. MOSCOU, R. A. PIEROTTI, J. ROUQUEROL and T. SIEMIENIEWSKA. 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure & Appl. Chem.* **57**: 603.
- WANG D., M. C. KUNG and H. H. KUNG. 2000. Oxidation of butane over vanadium-phosphorus oxides of P/V \geq 2. *Catal. Lett.* **65**: 9-17.