

PHYSICO-CHEMICAL CHARACTERIZATION OF VANADIUM-PHOSPHORUS-OXIDE CATALYSTS PREPARED IN ORGANIC AND AQUEOUS MEDIUM

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Abstract. Two vanadium-phosphorus oxide (VPO) catalysts were prepared by two different methods known as organic and aqueous medium. Characterization of these catalysts were carried out by BET surface area and porosity, gravimetry thermal analysis (TGA/DTG) and temperature programmed reduction (TPR). The results show that VPO catalyst prepared in organic medium gave larger surface area, higher lattice oxygen mobility and has a greater reduction site.

Key words: Vanadium-Phosphorus-Oxide, butane oxidation, maleic anhydride, temperature-programmed reduction.

Abstrak. Dua mangkin vanadium-fosforus-oksida (VPO) telah disediakan dengan menggunakan kaedah yang dikenali sebagai medium 'organik' dan 'akueus'. Pencirian mangkin ini telah dilakukan dengan menggunakan luas permukaan BET dan keliangan, analisis gravimetri terma (TGA/DTG) dan penurunan berprogram suhu (TPR). Hasil kajian menunjukkan mangkin VPO yang disediakan dalam media organik memiliki luas permukaan yang lebih besar, mobiliti oksigen kekisi yang lebih tinggi dan mempunyai tapak penurunan yang lebih banyak.

Kata kunci: Vanadium-fosforus-oksida, pengoksidaan butana, penurunan berprogram suhu

1.0 INTRODUCTION

Vanadium-phosphorus oxide (VPO) catalysts are well established as selective partial oxidation catalysts for the production of maleic anhydride from *n*-butane for over 25 years. In recent years, attention in the literature has focused mainly on vanadyl pyrophosphate, $(VO)_2P_2O_7$ which has an active centre that is proposed to be the (100) plane and is claimed as the active phase of industrial catalyst for the *n*-butane oxidation to maleic anhydride [1]. The catalyst is usually prepared via a multistep transformation of the precursor, $VOHPO_4 \cdot 0.5H_2O$ under catalytic condition [2]. A survey of the literature [3] indicates that the catalytic behaviour of the catalyst system depends entirely on the method of preparation.

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In this study VPO catalysts were prepared in two methods known as aqueous and organic medium. The physico-chemical properties of the catalysts were investigated using surface area and porosity measurements, TGA/DTG analysis and temperature programmed reduction (TPR).

2.0 EXPERIMENTAL

2.1 Catalyst Preparation

The VPO catalysts were prepared accordingly to the method so-called organic and aqueous medium.

(i) Preparation in an Organic Medium, VPO (org)

15 g of V_2O_5 (Sigma) was suspended by rapid stirring into 90 mL of isobutyl alcohol and 60 mL of benzyl alcohol. The vanadium oxide-alcohol mixture was refluxed for 3 hours at 120°C under continuous stirring. During this period the solution changed in colour from brown to black. The mixture was then cooled to room temperature and left stirring at this temperature overnight. 99% *o*- H_3PO_4 was added in a quantity such as to obtain the expected P:V atomic ratio. The resulting solution was again heated to 120°C and maintained under reflux with constant stirring for 2 hours. Then the slurry (precursor) was filtered, washed, and dried at 150°C . This precursor was calcined in air at 400°C for 6 hour and then for an additional 3 hour in a mixture of 0.75% *n*-butane and air.

(ii) Preparation in an Aqueous Medium, VPO (aq)

15 g of V_2O_5 (Sigma) was dissolved in 200 mL of 37% HCl. The solution was refluxed and stirred until complete reduction to vanadium (IV) (about 3 hours). Then 85% *o*- H_3PO_4 was added to obtain the desired P/V atomic ratio; at this stage, no precipitation occur because the solution is strongly acidic. This solution was allowed to boil for 2 hours and concentrated to a volume of 20 mL to which hot water was then added to obtain blue vanadyl orthophosphate. After evaporation, the solid (precursor) was dried at 150°C overnight, and then calcined as described in the previous method.

2.2 Catalysts Characterization

The total surface area and the porosity of the catalysts were measured by BET (Brunauer-Emmet-Teller) method using nitrogen adsorption-desorption at -196°C . This was done using a Micromeritics ASAP 2000.

TGA/DTG analysis experiments were performed with a DuPont model 990 instrument. The temperature was raised from ambient to 1000°C with a heating rate of $10^\circ\text{C min}^{-1}$ under the flow of N_2 .

TPR analysis was carried out with a Micromeritics 2900 TPD/TPR using 10% hydrogen in argon. The temperature was raised from ambient to 920°C with a heating rate of 20°C min⁻¹.

3.0 RESULTS AND DISCUSSION

3.1 Surface Area and Porosity

The BET surface area of VPO (org) and VPO (aq) obtained were 18.4 and 5.2 m² g⁻¹, respectively. The micropore area of VPO (org) is 1.9 m² g⁻¹ whereas for VPO (aq) is 0.98 m² g⁻¹. The catalyst prepared in an organic medium, VPO (org) gave a higher surface area compared to the one prepared in aqueous medium, VPO (aq). This result is in agreement with those reported earlier by Batis *et al.* [4] and, Cavani and Trifiro [5]. Both nitrogen adsorption-desorption isotherms of VPO (org) and VPO (aq) encountered are of Type II isotherms with the presence of hysteresis loop [6], indicating the presence of a mixture of porosity and mesopores. The hysteresis loop is a Type H2, indicating the presence of pore with ink-bottle shape or by pores having varying widths.

3.2 Thermogravimetric/Differential Thermogravimetry Analysis (TGA/DTG)

Figures 1 and 2 are the TGA/DTG analysis profile obtained by raising the temperature from ambient to 1000°C at 10°C min⁻¹ under N₂ stream for VPO (org) and

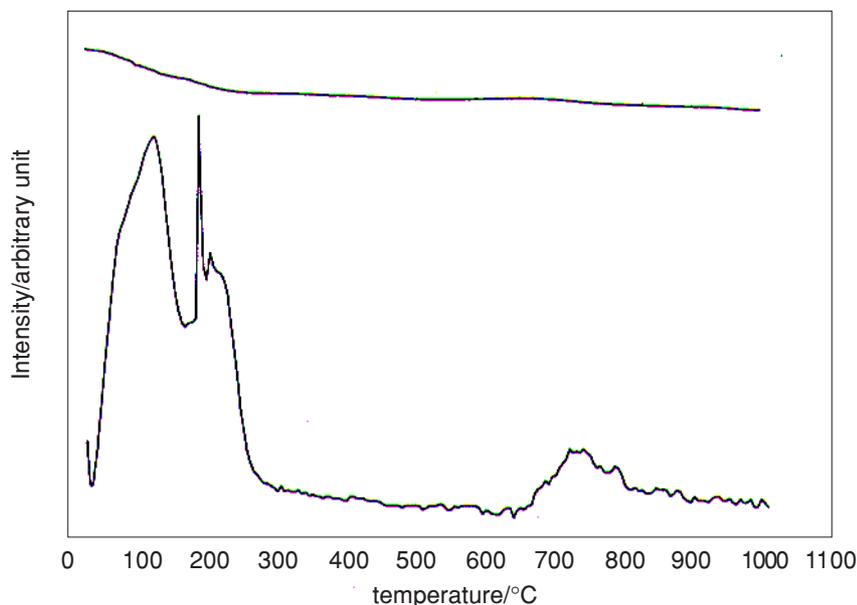


Figure 1 TGA/DTG thermogram of VPO (org)

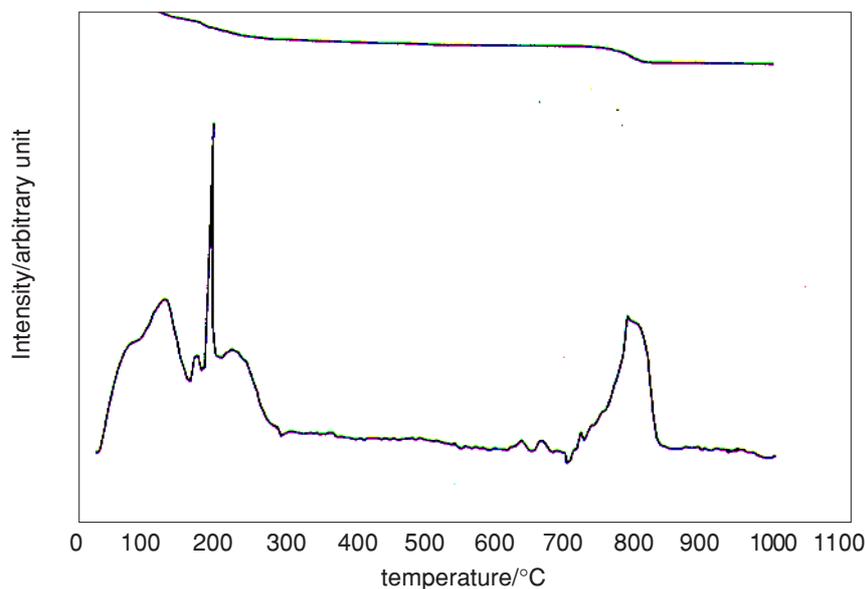


Figure 2 TGA/DTG thermogram of VPO (aq)

VPO (aq), respectively. Both figures gave a similar pattern of peaks below 300°C *i.e.* at 80 (shoulder), 130, 195 and 230°C. These peaks may correspond to weakly held surface water.

These two figures also show a peak at a higher temperature region. With an onset of evolution occurs at ~650°C, the rate desorption maximising at 750°C for organic prepared VPO catalyst, VPO (org), whereas VPO (aq) gave a higher peak maximum at 850°C with an onset occurs at ~750°C. Both individual peaks correspond to a total weight loss of ~1.6% and ~2.4% for VPO (org) and VPO (aq), respectively.

A comparison of both thermograms was made with the O₂ temperature programmed desorption (TPD) spectrum of (VO)₂P₂O₇ catalyst [7]. A peak which was observed at 750°C with a shoulder at 725°C in O₂ TPD spectrum are assigned to the desorption of lattice oxygen from the catalysts with a total amount of ~1% oxygen desorption. Therefore, the peaks at 750°C and 850°C shown in the thermograms, respectively are clearly related to the desorption of lattice oxygen from VPO (org) and VPO (aq). The exact amount of oxygen desorbed in this study was unable to be quantified due to these peaks were also included the desorption of CO and CO₂. However, the total amount of weight loss was found to be ~1–2% leading to the important conclusion that these peaks are the lattice oxygen.

The desorption activation energies of these strongly-bound oxygen species has been obtained by solution of the Redhead equation,

$$\frac{E_d}{RT_m^2} = \left(\frac{A}{\beta} \right) \exp \left(\frac{-E_d}{RT_m} \right)$$

where E_d is the desorption activation energy (J mol^{-1}), A is the desorption A -factor (10^{13} s^{-1} , assumed), R is the gas constant ($\text{JK}^{-1} \text{ mol}^{-1}$), β is the heating rate (Ks^{-1}) and T_m (K) is the temperature of the peak maximum. For peaks maxima at 750 and 850°C, desorption activation energies of 282 and 301 kJ mol^{-1} respectively, are obtained.

The significance of this result is that the VPO (org) catalyst has a higher mobility of lattice oxygen compared to VPO (aq) catalyst. This can be observed from (i) a lower desorption activation energy, E_d and (ii) a lower onset oxygen evolution. Our earlier results [7] show that this specific lattice oxygen is extremely selective for *n*-butane, but-1-ene and but-1,3-diene oxidation. This result also explain the reason for organic prepared VPO catalyst to be more active as compared to those prepared in aqueous medium.

3.3 Temperature Programmed Reduction (TPR)

Additional information as to the nature and the amount of oxidizing species available from the VPO catalysts were obtained by TPR in a H_2/Ar stream (10% H_2 , 50 mL min^{-1}) of a fresh sample of catalyst raising the temperature from ambient to 920°C at $20^\circ\text{C min}^{-1}$ in that stream. The TPR profile obtained is shown in figure 3.

Four distinct peaks maxima of VPO (org) were observed in the rate of hydrogen consumption at 516, 592, 754 and 859°C whereas VPO (aq) also gave four peaks at 597, 774, 832 and 886°C. The total amount of oxygen atom removed from VPO

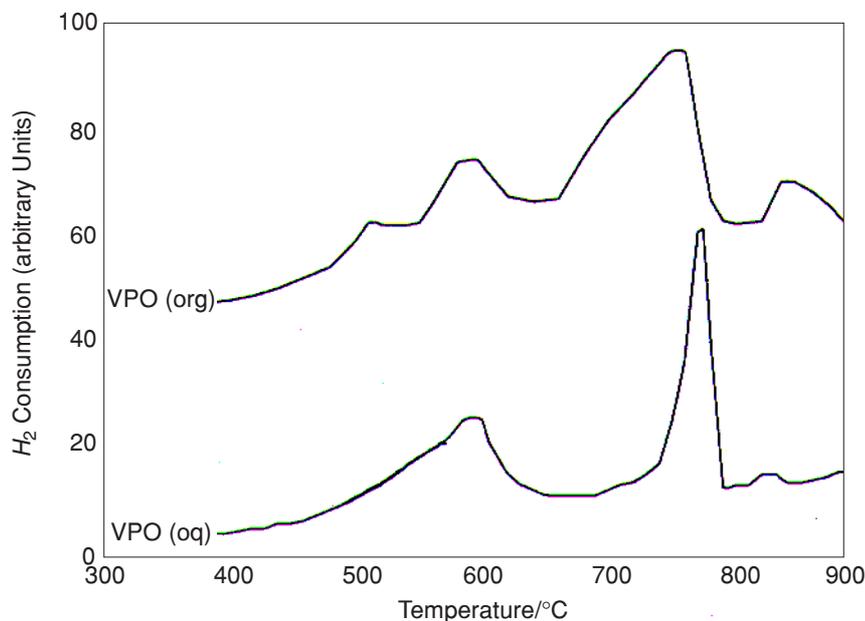
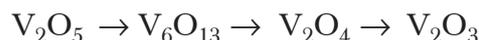


Figure 3 Temperature programmed reduction (TPR) of VPO (org) and VPO (aq)

(org) and VPO (aq) are 1.3×10^{21} atom g^{-1} and 2.6×10^{21} atom g^{-1} , respectively. This correspond to 5 and 11% respectively, of the total oxygen content released from the lattice of the catalysts.

Therefore, the peaks of these two catalysts observed in the rate of hydrogen consumption are in no way related to those observed by Koranne *et al.* [8] and by Bosch *et al.* [9] in the TPR of V_2O_5 catalyst which they ascribed to the



transformations.

The $\text{V}_2\text{O}_5 \rightarrow \text{V}_6\text{O}_{13}$ transformation alone accounted for 13% of the total oxygen. The amount of oxygen removed here suggests that it derives from the formation of extended surface and bulk defects [10]. Values of the activation energies for the reaction



where $\text{O}(\text{s})$ is the surface lattice oxygen species and \square is an oxygen vacancy site which can be obtained from a modified version of the Redhead equation,

$$\frac{E_r}{RT_m^2} = \left(\frac{A_r}{\beta} \right) [\text{H}]_m \exp\left(\frac{-E_r}{RT_m} \right)$$

where T_m is the peak maximum temperature (K) in the rate of H_2 consumption, E_r is the reduction activation energy (kJ mol^{-1}), A_r is the reduction pre-exponential term ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) which is given the value of a standard collision number of $10^{13} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$, β is the heating rate (K s^{-1}) and $[\text{H}]_m$ is the gas phase concentration of hydrogen (mol cm^{-3}) at the peak maximum. The E_r value for both catalysts are summarized in Table 1.

Table 1 Desorption activation energies obtained by temperature programmed reduction (TPR) for VPO (org) and VPO (aq)

VPO (org) $T_m/\text{°C}$	Desorption activation energy, E_d/kJmol^{-1}	VPO (aq) $T_m/\text{°C}$	Desorption activation energy, E_d/kJmol^{-1}
516	136.6	597	150.5
592	149.8	774	181.2
754	190.4	832	191.2
839	192.5	886	200.5

T_m = peak maximum temperature

4.0 CONCLUSIONS

The behaviour of the VPO catalyst is dependent upon the method of preparation. The catalyst prepared in an organic medium exhibit a higher surface area, lower desorption activation of oxygen which gave a higher mobility of lattice oxygen and bigger reduction site for oxidation of hydrocarbon.

5.0 ACKNOWLEDGEMENT

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