The effect of the duration of n-butane/air pretreatment on the morphology and reactivity of $(VO)_2P_2O_7$ catalysts

Y.H. Taufiq-Yap [a], M.H. Looi [a], K.C. Waugh [b], M.Z. Hussein [a], Z. Zainal [a] and R. Samsuddin [c]

[a] *Department of Chemistry, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
[b] *Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, UK*
[c] *Petronas Research, Scientific and Services Sdn. Bhd., Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Institusi Bangi, 43000, Kajang, Selangor, Malaysia*

Received 30 November 2000; accepted 23 March 2001

Three vanadium pyrophosphate catalysts have been prepared by calcining vanadium hydrogen phosphate hemihydrate ($VOHPO_4\cdot 0.5H_2O$, prepared in an organic medium) for different lengths of time (40, 100 and 132 h) in a n-butane (0.75%)/air mixture at 473 K. The catalysts were designated VPO40, VPO100 and VPO132. Increasing the duration of reaction with n-butane/air mixture led to an increase in the total surface area from 21.3 $m^2\,g^{-1}$ (VPO40) to 24.9 $m^2\,g^{-1}$ (VPO100) and to 27.0 $m^2\,g^{-1}$ (VPO132). It also led to the complete removal of the $VOPO_4$ phase from catalysts VPO100 and VPO132, this $VOPO_4$ phase having seen as a minor component of catalyst VPO40. Scanning electron microscopy showed that longer periods of pretreatment in the n-butane/air mixture produced catalysts with increasing amounts of a characteristic rosette-type of agglomerate. Temperature-programmed reduction with H_2 resulted in the removal of $\sim$11 monolayers equivalent of oxygen from all three of these catalysts at a peak maximum temperature of $\sim$1000 K with the development of a second reduction peak at $\sim$1100 K which increases with increasing time of n-butane/air pretreatment. The morphology produced by extended pretreatment in the n-butane/air mixture at 673 K is therefore predisposed to reaction with H_2 (and probably with n-butane). Apparently paradoxically, increasing the duration of n-butane/air pretreatment results in catalysts which on temperature-programmed desorption desorb less oxygen.

KEY WORDS: vanadyl pyrophosphate; XRD; SEM; oxygen; TPR; TPD

1. Introduction

Vanadium phosphorus oxides (VPO) catalysts are commercially used in industry for the selective oxidation of n-butane to maleic anhydride (MA). It is, so far, the only successful industrial process utilising alkanes [1]. In 1995, global production of maleic anhydride was estimated at 1.8 billion pounds, with an estimated value of USD 700 million. The consumption of maleic anhydride has been forecast to grow over the next five years at an average annual rate of 3.1% in the United States and Western Europe, 1.9% in Japan and 7–8% in Southeast Asia and China [2]. The low price and environmental neutrality of alkanes to produce a high-value product make this process extremely attractive [2,3].

The most active phase of VPO catalyst for synthesis of MA is made up of a well-crystallized $(VO)_2P_2O_7$ which is considered to possess unique structural and surface features to allow the activation of an alkane [4–7]. This phase is generally generated by a long-term calcination of the precursor, $VOHPO_4\cdot 0.5H_2O$ prepared in an organic solvent method followed by treatment in a reaction environment, *i.e.*, n-butane/air flow at 653–723 K. Transformation of precursor to the active phase can be affected by the temperature, time and atmosphere of treatment. Precursors calcined for a period less than 100 h will yield the so-called "non-equilibrated" catalysts, while a calcination time of more than 1000 h will yield the "equilibrated" catalysts, which are thermodynamically more stable under usual reaction conditions [4–6].

The purpose of this paper is to extend this earlier work by investigating the effect of the duration of calcination under reaction conditions upon $(VO)_2P_2O_7$ catalysts by means of various techniques, *i.e.*, BET surface area, XRD, SEM, TPD and TPR.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared in organic medium by the following procedure. Vanadium pentoxide, V_2O_5 (15.0 g from Fluka), was suspended by rapid stirring into a mixture of isobutyl alcohol (90 cm^3) and benzyl alcohol (60 cm^3). The vanadium oxide–alcohol mixture was refluxed for 3 h at 393 K, stirring throughout. The mixture was then cooled to room temperature overnight. H_3PO_4 (85%) was added in such a quantity to obtain the desired P : V atomic ratio. The resulting solution was again heated to 393 K and maintained under reflux with constant stirring for 2 h. The slurry was then filtered, washed and dried overnight in an oven at 423 K.

The resulting precursor, which was shown to be a well-crystallised $VOHPO_4\cdot 0.5H_2O$ (VPOPre) by X-ray diffraction analysis, was then calcined under a flow of n-butane/air

1011-372X/01/0600-0099$19.50/0

mixture (0.75% n-butane in air) at 673 K for 40, 100 and 132 h. The resulting catalysts were denoted by VPO40, VPO100 and VPO132, respectively.

2.2. Catalysts characterization

The total surface areas of the catalysts were measured by the BET (Brunauer–Emmer–Teller) method using nitrogen adsorption at 77 K. This was done using a Micromeritics ASAP 2000.

The X-ray diffraction (XRD) analyses were carried out using a Shimadzu diffractometer model XRD 6000 employing Cu K_α radiation to generate diffraction patterns from powder crystalline samples at ambient temperature.

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

TPD and TPR analysis were done using a Micromeritics 2900 TPD/TPR apparatus utilising a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Brunauer–Emmer–Teller (BET) surface area measurements

The surface areas of the catalysts are as follows: 21.3 $m^2\,g^{-1}$ for VPO40, 24.9 $m^2\,g^{-1}$ for VPO100 and 27.0 $m^2\,g^{-1}$ for VPO132. Raising the calcination time increased the surface area. These values are also higher than those reported by Abon *et al.* [6–8].

3.2. X-ray diffraction (XRD)

Study of the XRD spectrum of the precursor showed the presence of $VOHPO_4{\cdot}0.5H_2O$, which was characterized by peaks at $2\theta = 15.5°$, $19.6°$, $24.2°$, $27.1°$ and $30.4°$, as shown in figure 1(a). These patterns are in good agreement with those reported for the $VOHPO_4{\cdot}0.5H_2O$ phase [4,8,9]. The XRD patterns of the three catalysts which were prepared by calcination of the same precursor at 723 K under the flow of n-butane (0.75% n-butane in air) for different times on stream, *i.e.*, 40, 100 and 132 h, are presented in figure 1 (b), (c) and (d). These show that these catalysts have a well crystallised $(VO)_2P_2O_7$ phase. These materials are quite different from those obtained by Abon *et al.* [6–8], which are characteristic of a poorly crystallised $(VO)_2P_2O_7$ phase. However, our results are in agreement with those in which the amount of $(VO)_2P_2O_7$ phase increases with the activation time. A minor $VOPO_4$ phase is detected on VPO40 while it was not on VPO100 and VPO132. The presence of $(VO)_2P_2O_7$ is characterized by the pyrophosphate lines at $2\theta = 23°$, $28.45°$ and $29.94°$.

3.3. Scanning electron microscopy (SEM)

The results from scanning electron microscopy show the surface morphologies of the catalysts with different calcination time. The principal structures of the catalysts are the

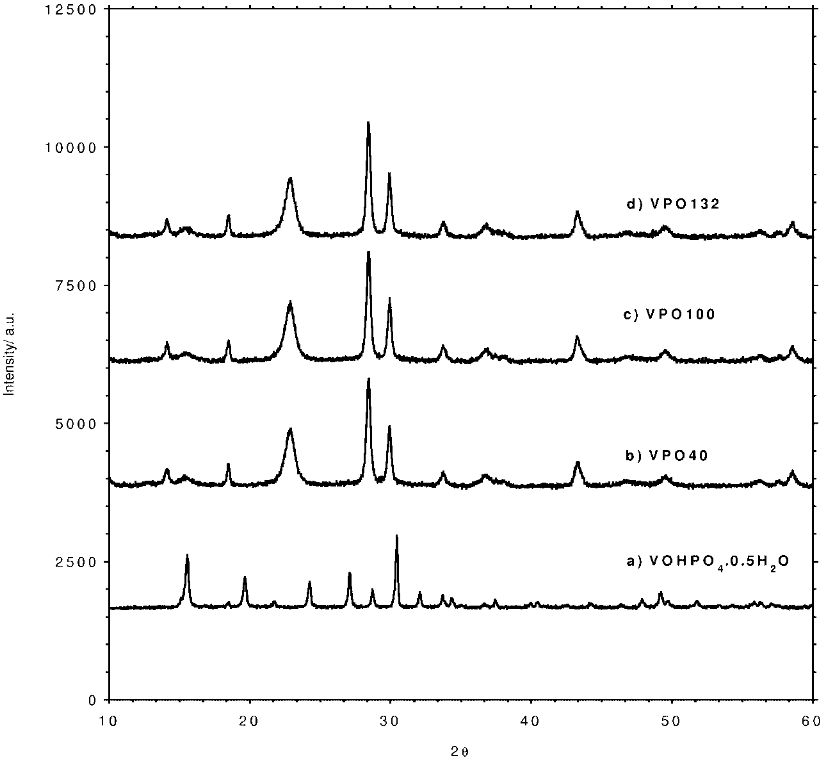
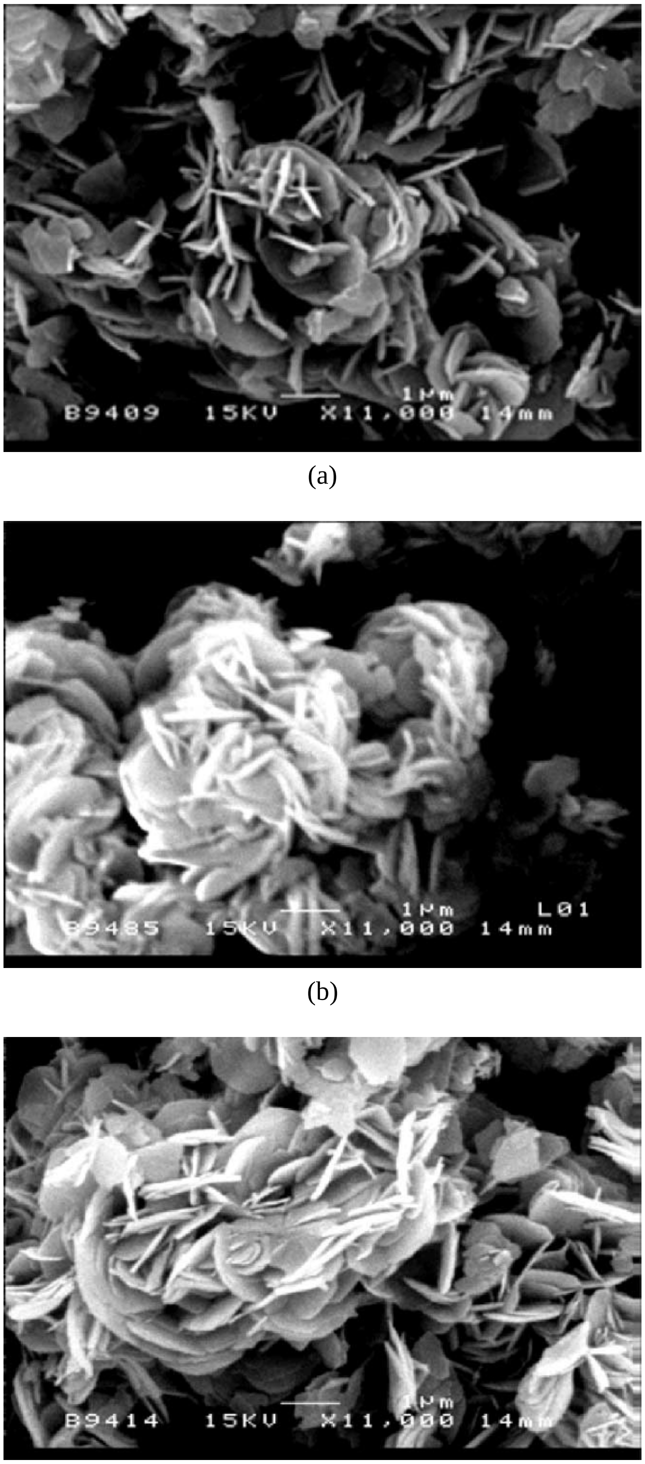


Figure 1. XRD patterns of VPO40, VPO100 and VPO132.



(a)

(b)

(c)

Figure 2. SEM micrograph of (a) VPO40, (b) VPO100 and (c) VPO132.

same: they consist of plate-like crystals, which are arranged into the characteristic rosette-shape clusters. However, the amounts of these characteristic rosette-type agglomerates are different in all of the catalysts, as shown in figures 2 (a), (b) and (c).

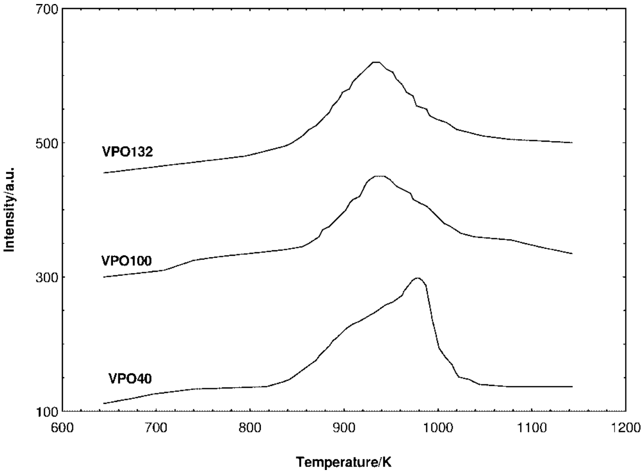


Figure 3. Oxygen TPD spectra of VPO40, VPO100 and VPO132.

The catalysts which had been calcined for the longest period of time, *i.e.*, VPO132, appeared to have clearer and more prominent rosette-shape agglomerates when compared to its less calcined counterparts. There appeared to be a consistency whereby the amount of these rosette-type agglomerates increased with increasing calcination time. The rosette-type agglomerates are made up of agglomerates of $(VO)_2P_2O_7$ platelets that preferentially expose (100) crystal planes [10]. The increase in the surface area for catalysts which had undergone a longer calcination time could be explained by the increase in the number of platelets which formed the rosette structure.

3.4. Oxygen desorption

The oxygen desorption spectra shown in figure 3 were obtained by pretreating the $(VO)_2P_2O_7$ catalysts by heating them to 673 K in an oxygen flow (101 kPa, 25 $cm^3\,min^{-1}$) and holding them under that flow at 673 K for 1 h before cooling them to ambient temperature. The flow was then switched to helium (1 bar, 25 $cm^3\,min^{-1}$) and the temperature was raised (10 $K\,min^{-1}$) to 1100 K following the conductivity of the eluted gas. Peaks obtained derived from the evolution of oxygen from the catalysts, it having been shown previously [11] that the pretreatment in oxygen at 673 K removed all the adsorbed H_2O. Peaks are observed at 978 K with a shoulder at 938 K for VPO40.

The total amount of oxygen desorbed is 2.0×10^{20} atom g^{-1} (table 1), and this is almost the same as we reported previously for a calcination of 6 h in a mixture of n-butane/air [12]. However, the desorption temperatures have been slightly reduced from 1023 and 998 K. This amount on a catalyst with surface area of 21.3 $m^2\,g^{-1}$, corresponds to a coverage of 9.4×10^{14} $atom\,cm^{-2}$ on the surface of the $(VO)_2P_2O_7$ catalyst. This coverage would correspond to more than a monolayer of chemisorbed oxygen.

For catalysts calcined for longer times (catalysts VPO100 and VPO132) two salient observations can be made. Firstly, the amount of oxygen desorbed is half that desorbed from catalyst VPO40, being 9.9×10^{19} for VPO100 and 1.0×10^{20} $atom\,g^{-1}$ for VPO132. This corresponds to coverages of 3.9×10^{14} and 3.7×10^{14} $atom\,cm^{-2}$ or the removal of

Table 1
Total number of oxygen atoms desorbed from the catalysts by O_2 TPD.

Catalyst[a]	T_{max} (K)	Oxygen atoms desorbed from the catalyst ($mol\,g^{-1}$)	Total oxygen atoms desorbed ($atom\,g^{-1}$)	Coverage ($atom\,cm^{-2}$)	Monolayers of oxygen removed[b]
VPO40	978	1.7×10^{-4}	2.0×10^{20}	9.4×10^{14}	1.3
	938				
VPO100	937	8.3×10^{-5}	9.9×10^{19}	3.9×10^{14}	0.6
VPO132	937	8.4×10^{-5}	1.0×10^{20}	3.7×10^{14}	0.5

[a] Surface area: VPO40 21.3 $m^2\,g^{-1}$, VPO100 24.9 $m^2\,g^{-1}$, VPO132 27.0 $m^2\,g^{-1}$.

[b] The monolayers of oxygen removed are calculated by dividing the oxygen coverage by 7×10^{14} $atom\,cm^{-2}$ – the stoichiometric value of monolayer oxygen coverage.

the equivalent of half a monolayer of the surface oxygen. The most likely route for this loss of oxygen from these catalysts is the formation of crystallographic shear planes [13]. This observation of the longer times of calcinations in the n-butane/air mixture producing catalysts which desorb less oxygen is consistent with one of the conclusions of a previous report, namely that the role of the n-butane/air pretreatment is to remove the unselective oxygen [11]; temperature-programmed reaction studies have shown that the shorter calcination time of 6 h leaves at least two monolayer equivalents of unselective oxygen [11]. Our conclusion that the n-butane/air pretreatment actually reduces the $(VO)_2P_2O_7$ catalyst accords with those of [14,15] who state that the plates formed by the n-butane/air pretreatment are actually reduced phases of VPO.

The second important point to note is that increasing the calcination time to 100 and 132 h results in the loss of high-temperature desorption state having a T_m of 978 K (and the concomitant loss in the total amount of oxygen desorbed); the low-temperature state ($T_m = 938$ K) remains in roughly the same amount.

The oxygen desorption peaks from catalysts VPO100 and VPO132 are symmetric and are therefore second order [16]. The rate of desorption is therefore given by

$$-\frac{d[O_{(s)}]}{dt} = Ae^{-E/RT}[O_{(s)}]^2, \qquad (1)$$

where $[O_{(s)}]$ is the surface oxygen atom concentration (molecule cm^{-2}), t is time (s), A is the Arrhenius pre-exponential term ($cm^2\,s^{-1}$), E is the desorption activation energy ($J\,mol^{-1}$), R is the gas constant ($J\,K^{-1}\,mol^{-1}$) and T is the temperature (K). Since the rate of desorption $-d[O_{(s)}]/dt$ is equal to the height of the peak, h (cm), at any temperature, T (K), multiplied by some calibration constant K', and since the surface oxygen atom concentration $[O_{(s)}]$ at that temperature is given by the area (cm^2) of the peak at that temperature multiplied by some other calibration constant K'', then equation (1) becomes

$$K'h = Ae^{-E/RT}(K''\ \text{area})^2 \qquad (2)$$

or

$$h/(\text{area})^2 = Ae^{-E/RT}\frac{K'}{(K'')^2}. \qquad (3)$$

A plot of $\ln(h/(\text{area})^2)$ versus $1/T$ constitutes line shape analysis of the peak and provides the desorption activation energy without the need for calibration or assumptions about the value of the desorption pre-exponential factor. The value so obtained is 97 $kJ\,mol^{-1}$.

3.5. Temperature-programmed reduction (TPR) in H_2/Ar

Additional information as to the nature and the oxidizing species available from the VPO catalysts was obtained by TPR in H_2/Ar stream (10% H_2) using a fresh sample of catalyst and raising the temperature from room temperature to 1173 K at 20 $K\,min^{-1}$ in that stream. The TPR profiles in H_2 so obtained are shown in figure 4. Table 2 lists the peak maximum temperatures, the amounts of oxygen removed in each peak and the derived reduction activation energies.

There are several points to note from these temperature-programmed reduction profiles. These are: (i) regardless of the duration of pretreatment in the n-butane/air mixture, the amount of oxygen removed by H_2 at the peak maximum of ∼1010 K is roughly the same; (ii) the amount of oxygen removed by H_2 in this peak is $\sim 2 \times 10^{20}$ $atom\,g^{-1}$ (equivalent to 11 monolayers) which is a factor of 10 greater than that removed by thermal desorption for catalyst VPO40 and 20 greater that that removed by TPD from catalysts VPO100 and VPO132; (iii) while reaction with H_2 induces the removal of a greater amount of oxygen from the lattice than can be removed thermally, the peak maximum temperature of the reduction is higher than that of the thermally induced desorption, suggesting that the rate-determining step in both is the diffusion of oxygen through the lattice (the line shapes of the H_2-TPR peaks shown in figure 4 are characteristic of zero-order reaction [17]), exhibiting an exponentially increasing edge and a near-vertical decrease after the maximum. This conclusion of the reaction being zero order is consistent with the large amount of oxygen removed from the lattice (11 monolayers equivalent). A plot, therefore, of the logarithm of the rate of reaction (peak height) versus $1/T$ constitutes line shape analysis of this peak; it provides an activation energy of 119 $kJ\,mol^{-1}$ for reduction of the catalyst by H_2. This value is the same for all three catalysts so that varying the time of pretreatment in the n-butane/air mixture has no effect on the kinetics of the reduction of this phase; (iv) increasing the duration of the n-butane/air pretreatment from 40 to 100 h and 132 h results in the development of a new peak at 1100 K in the

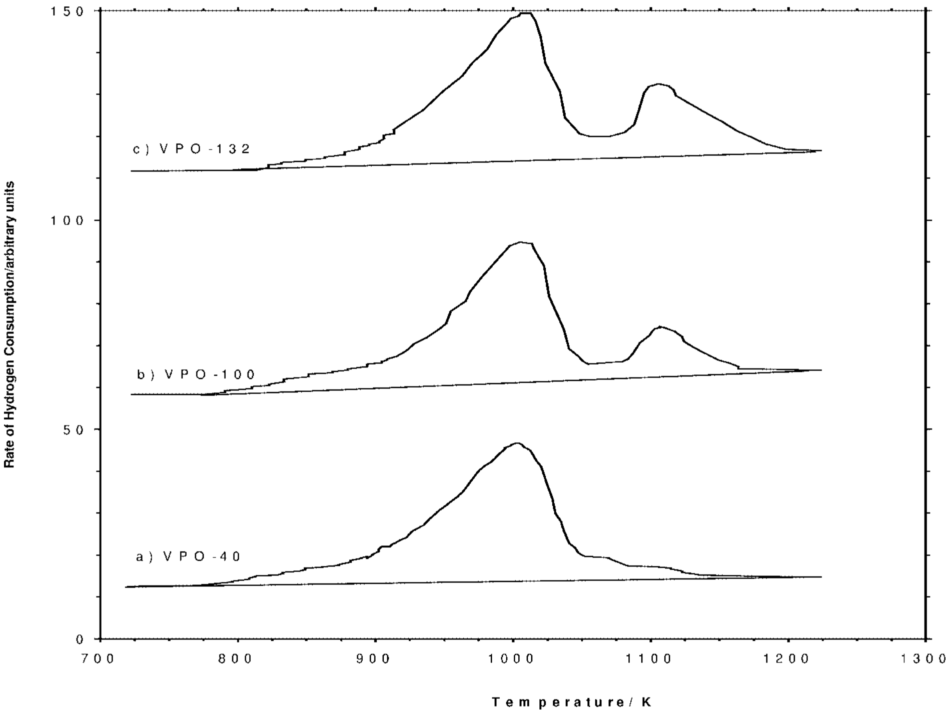


Figure 4. H_2-TPR spectra of VPO40, VPO100 and VPO132.

Table 2

Total number of oxygen atoms removed from VPO40, VPO100 and VPO132 catalysts by reduction in H_2/Ar.

Peaks[a]	T_{max} (K)	Reduction activation energy E_r (kJ mol^{-1})	Oxygen atoms removed from the catalyst (mol g^{-1})	Oxygen atoms removed from the catalyst (atom g^{-1})	Coverage (atom cm^{-2})	Monolayers of oxygen removed[b]
VPO40						
1	1003	174	2.7×10^{-3}	1.6×10^{21}	7.7×10^{15}	11.0
VPO100						
1	1009	175	3.3×10^{-3}	2.0×10^{21}	8.0×10^{15}	11.0
2	1109	192	7.3×10^{-4}	4.4×10^{20}	1.8×10^{15}	2.6
Total oxygen atoms removed			4.0×10^{-3}	2.4×10^{21}	9.8×10^{15}	13.6
VPO132						
1	1009	175	3.7×10^{-3}	2.2×10^{21}	8.1×10^{15}	11.0
2	1109	192	1.2×10^{-3}	7.4×10^{20}	2.7×10^{15}	3.9
Total oxygen atoms removed			4.9×10^{-3}	2.9×10^{21}	1.1×10^{16}	14.9

[a] Surface area: VPO40 21.3 m^2 g^{-1}, VPO100 24.9 m^2 g^{-1}, VPO132 27.0 m^2 g^{-1}. Weight of catalyst = 0.03 g.

[b] The monolayers of oxygen removed are calculated by dividing the oxygen coverage by 7×10^{14} atom cm^{-2} – the stoichiometric value of monolayer oxygen coverage.

H_2-TPR profile; (v) the amount of oxygen removed in this high-temperature state increases with an increase in the duration of the *n*-butane/air pretreatment, having a value of 4.4×10^{20} atom g^{-1} (2.6 monolayer equivalent) for 100 h pretreatment, rising to 7.4×10^{20} atom g^{-1} (3.9 monolayer equivalent) for 132 h pretreatment.

The result that the longer the period of *n*-butane/air pretreatment the more oxygen is removed from the lattice by reaction with H_2 appears to conflict with the observation that less oxygen is available from the lattice thermally on increasing the time of *n*-butane/air pretreatment. However, it is clear from the fact that reduction in H_2 removes >10 times the amount of lattice oxygen which can be removed thermally, that the transition states of the two processes are quite different. The SEM pictures in figure 2 show that treatment in the *n*-butane/air mixtures for different periods of time produces totally different surface morphologies. The surface and bulk morphologies produced by pretreatment in the *n*-butane/air mixture for 132 h is self evidently more reactive toward H_2 than those produced by shorter periods *n*-butane/air pretreatment. The surface/bulk morphologies of the catalysts VPO40, VPO100 and VPO132 are largely the same, evidenced by the same amount of oxygen being removed by H_2 at 1010 K for all three catalysts. However, a new phase is formed upon longer treatments in the *n*-butane/air mixture which reacts with H_2 at an onset temperature of 1100 K. This phase and the additional amount of oxygen it provides from the lattice might well be the source of the higher selectivity produced by longer periods of *n*-butane/air pretreatment.

4. Conclusions

(1) Increasing the length of time of pretreatment of vanadyl pyrophosphate catalysts to a *n*-butane/air mixture (0.75% *n*-butane) at 673 K increases the surface area of the catalyst and changes the surface and bulk morphologies into one in which more oxygen can be removed from the lattice by reaction with H_2.

(2) The significant difference between the catalysts produced for the longest time of pretreatment (132 h) and the shortest (40 h) is that the longest time of pretreatment produces a new phase which reacts with H_2 at an onset temperature of 1100 K in addition to the majority phase which is present in all catalysts whatever time of exposure to the *n*-butane/air mixture. This phase reacts with H_2 at an onset temperature of 800 K and with identical kinetics for all three catalysts.

(3) Apparently paradoxically, the least amount of oxygen can be removed from the catalysts thermally for the longest period *n*-butane/air pretreatment. This difference is rationalized in the markedly different transition state required for thermal evolution of O_2 compared with that for H_2 reduction of the surface, a fact borne out by the observation that H_2 reduction removes >10 times the oxygen from the lattice than is available thermally.

(4) H_2 temperature-programmed reduction is therefore a more reliable method of evaluation of catalysts for partial oxidation reactions.

Acknowledgement

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

References

[1] Catal. Today 16 (1993) 1–153 (the entire volume).
[2] G. Elvira and O. Beatrix, *Chemical Economics Handbook* (SRI Consulting, 1999).
[3] K. Wohlfahrt and G. Emig, Hydrocarbon Process. 83 (June 1980).
[4] S. Albonetti, F. Cavani, F. Trifirò, P. Venturoli, G. Calestani, M.L. Granados and J.L.G. Fierro, J. Catal. 160 (1996) 52.
[5] M.L. Granados, J.L.G. Fierro, F. Cavani, A. Colombo, F. Giuntoli and F. Trifirò, Catal. Today 40 (1998) 251.
[6] M. Abon and J.-C. Volta, Appl. Catal. 157 (1997) 173.
[7] M. Abon, K.E. Bere, A. Tuel and P. Delichere, J. Catal. 156 (1995) 28.
[8] J.M. Hermann, P. Vernoux, K. Bere and M. Abon, J. Catal. 167 (1997) 106
[9] N.H. Batis, H. Batis, A. Ghorbel, J.C. Vedrine and J.C. Volta, J. Catal. 128 (1991) 248.
[10] C.J. Kiely, S. Sajip, I.J. Ellison, M.T. Sananes, G.J. Hutchings and J. Volta, Catal. Lett. 33 (1995) 357.
[11] B.H. Sakakini, Y.H. Taufiq-Yap and K.C. Waugh, J. Catal. 189 (2000) 253.
[12] Y.H. Taufiq-Yap, B.H. Sakakini and K.C. Waugh, Catal. Lett. 46 (1997) 273.
[13] P.L. Gai and K. Kourtakis, Science 67 (1995) 661.
[14] P.L. Gai, Acta Cryst. B 53 (1997) 346.
[15] P.L. Gai, K. Kourtakis, D.R. Coulson and G.C. Sonnichsen, J. Phys. Chem. 101 (1997) 9916.
[16] P.A. Redhead, Vacuum 12 (1962) 203.
[17] R.J. Madix, Catal. Rev. Sci. Eng. 15 (1977) 293.