Catalysis Letters 46 (1997) 273–277

On the mechanism of the selective oxidation of *n*-butane, but-1-ene and but-1,3-diene to maleic anhydride over a vanadyl pyrophosphate catalyst

Y.H. Taufiq-Yap, B.H. Sakakini and K.C. Waugh

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88,
Manchester M60 1QD, UK

Received 4 March 1997; accepted 2 May 1997

The mechanism of the selective partial oxidation of *n*-butane, but-1-ene and but-1,3-diene over a vanadyl phosphate catalyst has been investigated by temperature-programmed desorption (TPD) and by anaerobic temperature-programmed oxidation (TPO). TPD showed lattice oxygen to be desorbed in two states at 998 and 1023 K. The anaerobic TPO of *n*-butane produced butene and butadiene at 1020 K; anaerobic TPO of but-1-ene produced butadiene and furan at 990 K and dehydrofuran at 965 K, while anaerobic TPO of but-1,3-diene produced dehydrofuran at 970 K, furan at 1002 K and maleic anhydride at 1148 K. The total amount of oxygen removed from the lattice in these anaerobic selective partial oxidations was the same as that evolved from the vanadyl phosphate catalyst by TPD. This, and the fact that the selective oxidation reactions occurred at the same temperature at which the oxygen evolves from the lattice, suggests that the lattice oxygen is uniquely selective when it appears at the surface of the catalyst. (Under identical conditions of flow rate, weight of catalyst, heating rate etc., the reaction of *n*-butane or of but-1,3-diene in air produced only CO_2 and H_2O.)

Keywords: C_4 hydrocarbons, oxidation, VPO catalyst

1. Introduction

In the partial air oxidation of hydrocarbons, e.g. benzene, butane, butene, over vanadium-based catalysts (V_2O_5/MoO_3 (3 : 1) for benzene and $(VO)_2P_2O_7$ for butane and butene), the fact that six or seven out of ten of the hydrocarbon molecules which react are converted to maleic anhydride continues to defy a comprehensive explanation. In the oxidation of benzene, the high selectivity was ascribed to two successive para additions of the molecular oxygen anion, O_2^-, across the benzene ring producing first hydroquinone and then maleic anhydride [1–3]. For butene, the selective oxidant is believed to be the lattice oxygen of the $(VO)_2P_2O_7$ crystal. Its high selectivity is thought to originate from the unique configuration of the butene, adsorbed on the (100) face of the $(VO)_2P_2O_7$ crystal, this configuration being produced by the adsorbing butene molecule being "chemically polarised" by the surface crystal field [4–6].

These then are the extremes of the postulates: (i) the molecular oxygen anion, O_2^-, is the selective oxidant with the configuration of the adsorbate playing some role in influencing the selectivity [1–3] and (ii) lattice oxygen is the oxidant with the configuration of the adsorbate being of paramount importance [4–6].

Recently, Dupont have reported selectivities of ~ 80% in the anaerobic partial oxidation of butane to maleic anhydride over $(VO)_2P_2O_7$ [7,8]. This has been achieved in a highly unconventional plant in which the $(VO)_2P_2O_7$ is oxidised in one reactor at 673 K. The catalyst is then transferred to a second reactor where a C_4H_{10}/N_2 mixture is passed over it at 630 K [8]. It is undoubtedly the oxygen of the $(VO)_2P_2O_7$ lattice and not chemisorbed oxygen which is responsible for this highly selective oxidation of butane. This is confirmed by consideration of the amount of oxygen involved in the reaction; it is 1–2% of the total lattice oxygen which is equivalent to roughly two monolayers of molecular oxygen [9]. The reduced (anion defected) catalyst is then transferred back to the oxidising reactor for regeneration.

The purpose of this paper is to investigate the kinetics and mechanism of the anaerobic partial oxidation of *n*-butane, but-1-ene and but-1,3-diene over a $(VO)_2P_2O_7$ catalyst and to determine the role of the lattice oxygen of the $(VO)_2P_2O_7$ catalyst in these partial oxidations.

2. Experimental

Catalyst preparation. The catalyst, vanadyl pyrophosphate, $(VO)_2P_2O_7$, with $P/V = 1.03$ was prepared in organic medium. V_2O_5 (15.00 g from Sigma) was suspended by rapid stirring into isobutyl alcohol (90 cm^3) and benzyl alcohol (60 cm^3). The vanadium oxide–alcohol mixture was refluxed for 3 h at 390 K, stirring throughout. 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. Ortho-phosphoric acid (99%) was

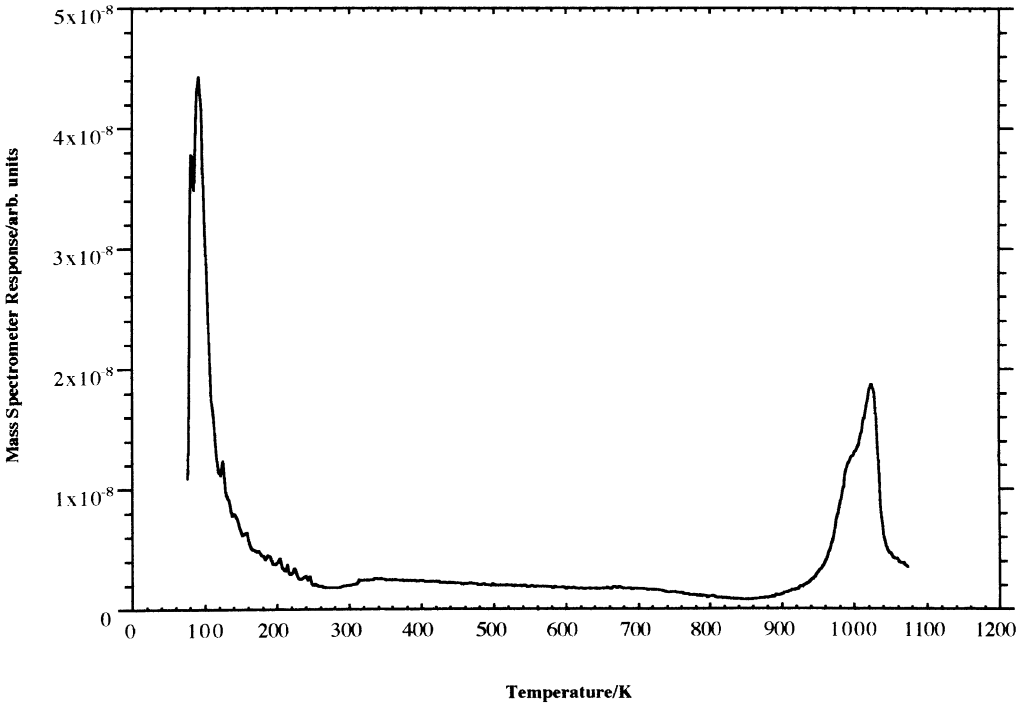

Figure 1. Temperature-programmed desorption of oxygen from the $(VO)_2P_2O_7$ catalyst.

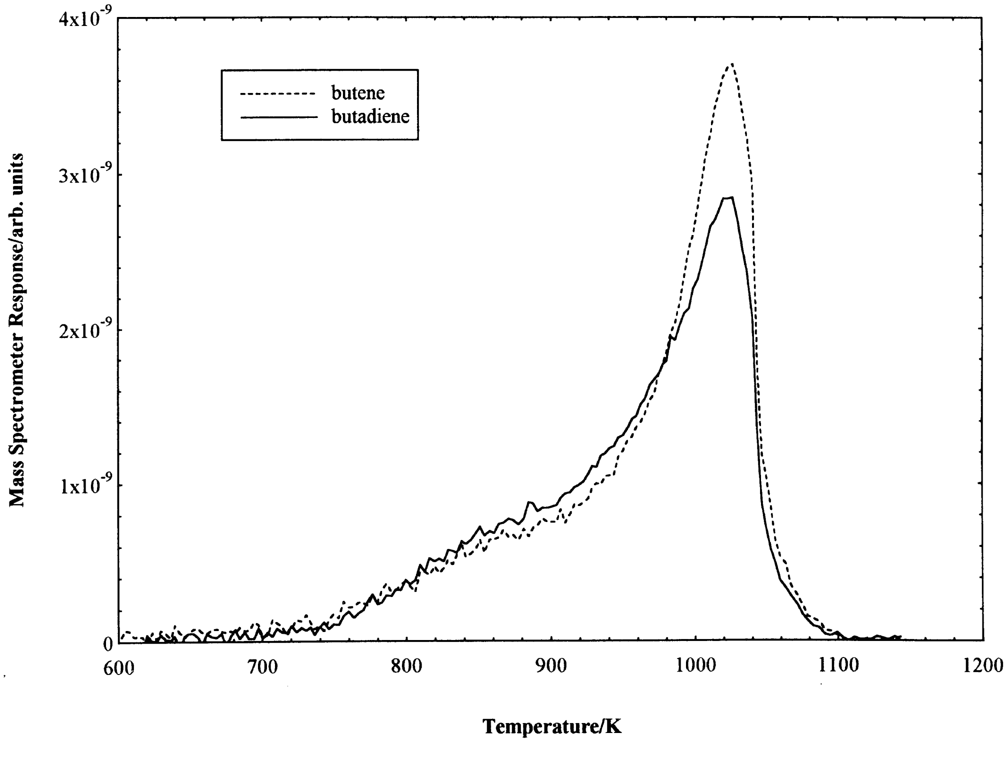

Figure 2. Anaerobic temperature-programmed oxidation of *n*-butane over the $(VO)_2P_2O_7$ catalyst.

added in such quantity as to obtain the desired P : V atomic ratio. The resulting solution was again heated to 390 K and maintained under reflux with constant stirring for 2 h. During this time, a reduced vanadium phosphate (probably 4+) was formed; this was indicated by a change in colour from black to blue. The slurry was then filtered, washed, and dried at 150°C. The precursor was then calcined for 6 h in a mixture of *n*-butane/air (0.75% *n*-butane in air) at 673 K a pretreatment which is considered to transform the catalyst into its most highly selective morphology (HSM) [10]. The solid recovered was shown to be pure $(VO)_2P_2O_7$ by chemical, infrared, and X-ray diffraction analysis. The surface area of this catalyst was measured in situ to be 24 $m^2\ g^{-1}$.

The gases. The gases, O_2 and He (British Oxygen Company), but-1-ene (5.03% in He (ECM), but-1,3-diene (5.14% in He (ECM)) and *n*-butane (0.75% in air (BOC)) were 99.9995 pure and were used direct from the cylinder.

The apparatus. TPD, TPR, TPO and TPRn experiments were conducted using a multipurpose microreactor system, described in detail previously [11,12]. This system basically consisted of a gas handling panel, a tubular reactor and a quadrupole mass spectrometer (Hiden Analytical, Warrington, England) which was capable of monitoring 16 masses continuously with temperature and time. The reactor was constructed of stainless steel tube (20 cm long, 0.4 cm i.d.) connected via heated capillary to the mass spectrometer. The catalyst, in the form of powder (typically 0.4–0.5 g) was placed in the reactor which could be cooled in a flow of liquid nitrogen to 77 K and heated in a temperature-programmed mode from that temperature to 1100 K using a Newtronics controller. The thermocouple used for temperature measurement and control was embedded in the catalyst.

3. Results and discussion

3.1. Oxygen desorption

The oxygen desorption spectrum shown in figure 1 was obtained by pretreating the HSM catalyst by heating it to 673 K in an oxygen flow (1 bar, 25 $cm^3\ min^{-1}$), holding it under that flow at 673 K for 1 h, before cooling it to 77 K. 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 $m/z = 32$ signal on the mass spectrometer. Peaks are observed at 83, 91 and 1023 K with a shoulder at 998 K. The peaks at 83 and 91 K correspond to desorption activation energies of 23 and 25 kJ mol^{-1}. This is physisorbed oxygen. The shoulder at 998 K and the peak at 1023 K correspond to desorption activation energies of 256 and 282 kJ mol^{-1}. The total amount of oxygen desorbed is 2.2×10^{20} atom g^{-1} which, on a catalyst whose surface area is 24 $m^2\ g^{-1}$, corresponds to more than a monolayer of chemisorbed oxygen. It is therefore lattice oxygen, the total amount desorbing being ~ 1% of the lattice oxygen, which is approximately the amount involved in the anaerobic industrial process [9].

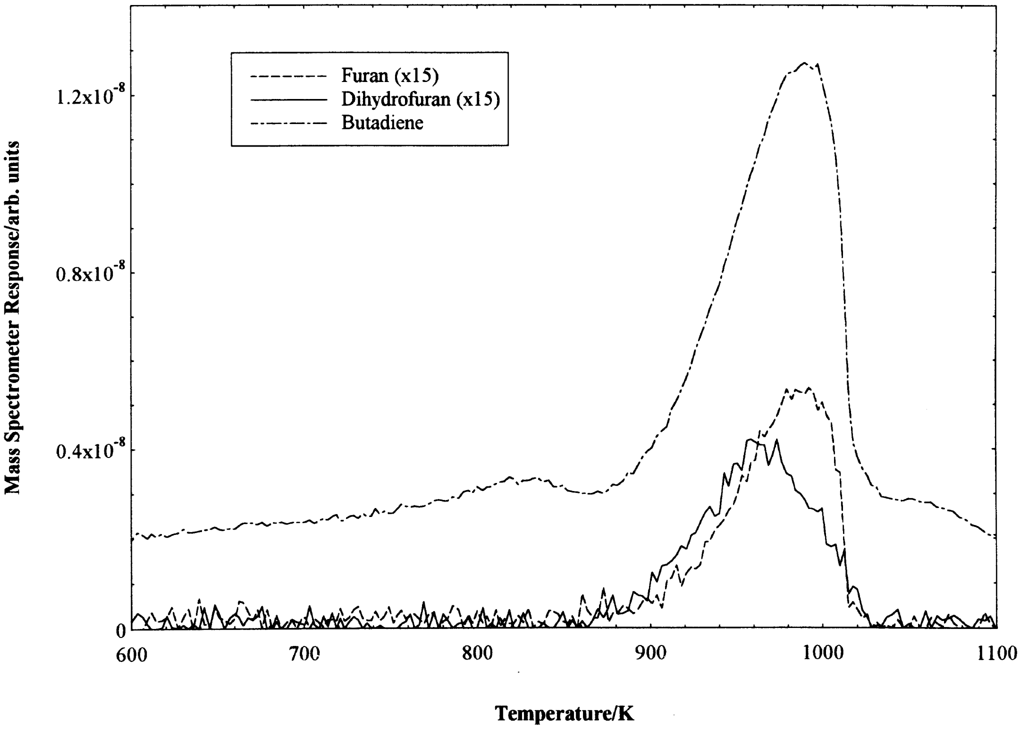

Figure 3. Anaerobic temperature-programmed oxidation of but-1-ene over the $(VO)_2P_2O_7$ catalyst.

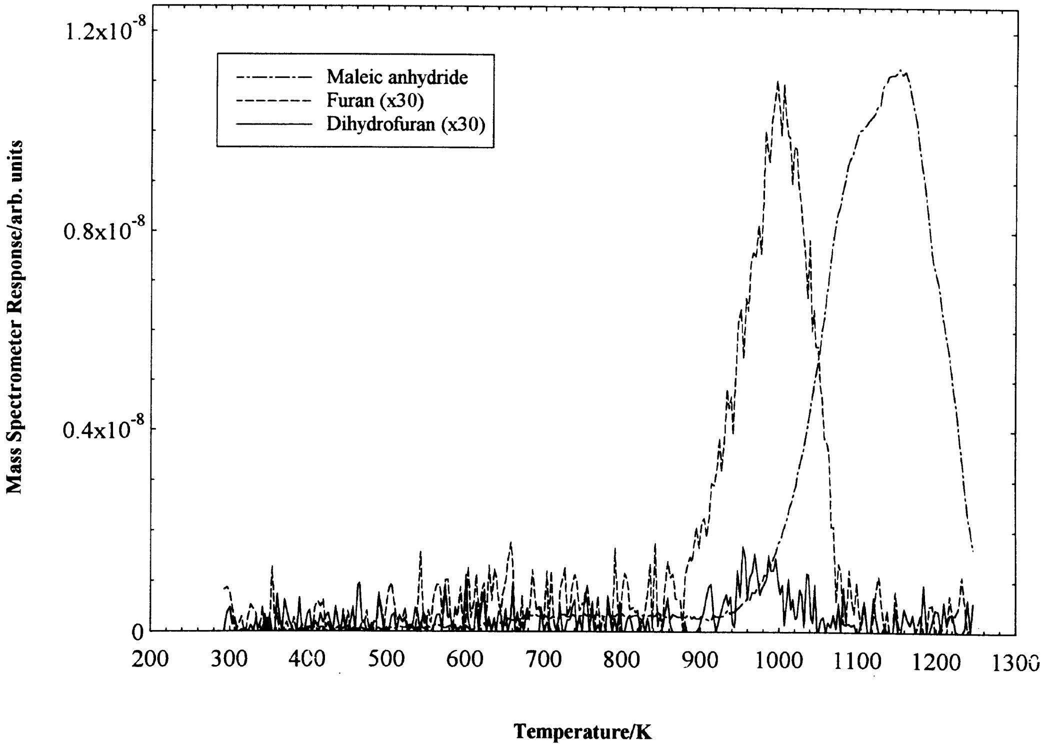

Figure 4. Anaerobic temperature-programmed oxidation of but-1,3-diene over the $(VO)_2P_2O_7$ catalyst.

3.2. Anaerobic temperature-programmed oxidation of n-butane, but-1-ene and but-1,3-diene over vanadyl pyrophosphate

Figure 2 is the temperature-programmed reaction profile obtained when a butane /He stream (1.85% butane, 1 bar, 25 cm^3 min^{-1}) is passed over the $(VO)_2P_2O_7$ (HSM) catalyst, raising the temperature from ambient to 1150 K at 5 K min^{-1}. Figure 3 is the profile obtained when the experiment is repeated on a fresh sample of the HSM catalyst using a but-1-ene/He stream (5.03% but-1-ene, 25 cm^3 min^{-1}) and figure 4 is the profile obtained using a but-1,3-diene/He (5.14% but-1,3-diene) also on a fresh sample of the HSM catalyst.

Using a butane feed the selective products obtained are butene and butadiene, the rate of production of each of these maximising at 1020 K, the temperature of the desorption maximum of the lattice oxygen. The quantity of oxygen involved in the production of the amounts of butene and butadiene shown in figure 2 is slightly larger than that evolved from the lattice of the $(VO)_2P_2O_7$ in the oxygen desorption spectrum shown in figure 1 (the m/z ratios used to identify the products are listed in table 1 while table 2 lists the quantities of products formed).

When but-1-ene is the feed, the selective products are butadiene (predominantly), furan and dihydrofuran, the furan appearing to be formed coincidentally with butadiene, having a maximum at 990 K, but at a slightly higher temperature than dihydrofuran whose maximum is at 965 K (figure 3). Using but-1,3-diene, the selective products obtained are furan (at 993 K), a small amount of dihydrofuran and an unquantifiable amount of maleic anhydride at 1148 K (figure 4). This lack of quantification of the amount of maleic anhydride produced was due to our inability to introduce a calibrated quantity of it into the mass spectrometer.

Table 1
The m/z ratios followed to identify the compounds cited

Compound	m/z followed	Comment
n-butane	43	unique
but-1-ene	41	(contribution from butane of 30% of the $m/z = 43$ peak)
but-1,3-diene	39 and 54	
2,5-dihydrofuran (DHF)	70	unique to DHF
furan	68	(2% contribution from DHF)
maleic anhydride	26	(contributions from all of above except DHF)

Table 2
Amounts of products formed in anaerobic temperature-programmed oxidation of *n*-butane, but-1-ene and 1,3-butadiene lattice on a $(VO)_2P_2O_7$ catalyst

Reactant	Products	T_{max} (K)	Amount of products (molecule g^{-1})	Lattice oxygen requirements for products (atom g^{-1})		Lattice oxygen desorbed (atom g^{-1})
n-butane	butene	1020	1.2×10^{20}	1.2×10^{20}	3.0×10^{20}	2.2×10^{20}
	butadiene	1020	0.9×10^{20}	1.8×10^{20}		
but-1-ene	butadiene	990	1.2×10^{20}	1.2×10^{20}	3.0×10^{20}	2.2×10^{20}
	dihydrofuran	965	0.6×10^{20}	1.2×10^{20}		
	furan	990	0.2×10^{20}	0.6×10^{20}		
but-1,3-diene	dihydrofuran	970	0.1×10^{20}	0.1×10^{20}	0.7×10^{20}	2.2×10^{20}
	furan	1002	0.3×10^{20}	0.6×10^{20}		
	maleic anhydride	1148	unquantified	–		

The selective partial oxidation products formed using either *n*-butane or but-1-ene consume exactly the same amounts of lattice oxygen, an amount which is the same (i.e. within the experimental error) of that which desorbs from the $(VO)_2P_2O_7$ lattice. (For reasons explained above the amount of lattice oxygen used in the selective partial oxidation of but-1,3-diene cannot be quantified.) In addition, the temperature regime in which all of the selective partial oxidation products are formed coincides with that in which molecular oxygen is evolved from the $(VO)_2P_2O_7$ lattice.

Under identical conditions of flow rate, weight of catalyst and heating rate, the reaction of *n*-butane, but-1-ene or 1,3-butadiene in air (0.75% hydrocarbon in air) produced only H_2O and CO_2.

These data lead to the following ineluctable conclusions: (i) that the mechanism of the partial oxidation of *n*-butane to maleic anhydride on $(VO)_2P_2O_7$ is *n*-butane → but-1-ene → but-1,3-diene → dihydrofuran → furan → maleic anhydride, (ii) that the oxygen from the lattice of the $(VO)_2P_2O_7$ catalyst when it evolves at the surface of the catalyst is, for some as yet unspecified reason, uniquely selective in the partial oxidation of butane and butenes and (iii) its appearance at the surface is the rate-determining step in these partial oxidations. This selective lattice oxygen which evolves as a distinct pulse at 1000 K will have a slow rate of evolution at 630 K, the temperature used industrially. Compensation for its slow rate of evolution at the industrial temperature is made in the longer contact times used industrially.

References

[1] J. Lucas, H.D. Vandervell and K.C. Waugh, J. Chem. Soc. Faraday Trans. I 77 (1981) 15.

[2] J. Lucas, H.D. Vandervell and K.C. Waugh, J. Chem. Soc. Faraday Trans. I 77 (1981) 31.

[3] R.W. Petts and K.C. Waugh, J. Chem. Soc. Faraday Trans. I 78 (1982) 803.

[4] J. Ziolotkowski, E. Bordes and P. Courtine, J. Catal. 122 (1990) 126.

[5] J. Ziolotkowski, E. Bordes and P. Courtine, Stud. Sci. Surf. Catal. 55 (1991) 625.

[6] J. Ziolotkowski, E. Bordes and P. Courtine, J. Mol. Catal. 84 (1993) 307.

[7] J.J. Lerou and Ph. Mills, in: *Precision Process Technology*, eds. M.P.C. Weijnen and A.A. Drinkenburg (Kluwer Academic, Dordrecht, 1993) p. 175.

[8] J.J. Lerou and K.M. Ng, Chem. Eng. Sci. 51 (1996) 1595.

[9] J.J. Lerou, private communication.

[10] G. Busca, G. Centi, F. Trifirò and V. Lorenzelli, J. Phys. Chem. 90 (1986) 1337.

[11] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.

[12] K.C. Waugh, Appl. Catal. 43 (1988) 315.

[13] G. Centi, J.L. Nieto, F. Ungarelli and F. Trifirò, Catal. Lett. 4 (1990) 309.

[14] F. Cavani and F. Trifirò, *Catalysis*, Vol. II (Royal Society of Chemistry, Cambridge, 1994) p. 246.