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Oxidation of butane to maleic anhydride using vanadium phosphate catalysts: comparison of operation in aerobic and anaerobic conditions using a gas-gas periodic flow reactor

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The use of a periodic flow reactor is described for the oxidation of butane to maleic anhydride to compare the catalytic performance of vanadium phosphate catalysts operating under aerobic and anaerobic conditions. It is found that for the catalyst prepared via a standard VPO method, operation in the absence of oxygen leads to a very small enhancement in selectivity when butane concentrations in the range 0.9–2.9% are used. Operation in the absence of oxygen leads to very small differences in conversion such that the overall yield is enhanced and this effect is maximised for reactor feeds containing 1.5% butane. However, the enhancement is negligible when the catalyst is operated at high conversion required for commercial operation, indicating that reactors operating with continuous flow with aerobic conditions are preferred. Similar experiments are conducted for a catalyst prepared by the VPD method and, in contrast, this catalyst gives lower butane conversion and maleic anhydride selectivity when operated in the absence of oxygen.

KEY WORDS: vanadium phosphate; butane oxidation; maleic anhydride; periodic flow.

1. Introduction

The oxidation of butane to maleic anhydride has become one of the most studied heterogeneously catalysed processes [1–6]. In early work on this reaction, operation of these catalysts used a continuous feed mode in which the butane is fed together with oxygen, or air, through a packed bed of the catalyst. Typically, the concentration of butane is below the lower explosion limit [5]. In an alternative approach, Contractor and co-workers [7–11] have developed the riser/circulating fluidised bed (CFB) reactor for this oxidation reaction, and this process is based on the observation that many oxides operate as oxidation catalysts by a Mars–van Krevelen mechanism, i.e. in the absence of a co-fed oxidant, the hydrocarbon reacts to give the selective oxidation product by reacting with lattice oxygen (O^{2-}) located at defect sites. In the CFB process, butane is reacted with the vanadium phosphate catalyst in the absence of air in a riser reactor. This permits the catalyst and hydrocarbon to remain in contact for a few seconds at the reaction temperature. Subsequently, the reaction products are recovered and the catalyst is re-oxidised in a fluidised bed by reaction with air. Decoupling the catalyst reduction and re-oxidation stages of the catalyst operation leads to improved process control; however, it does not lead to the elimination of the formation of CO_2 as a nondesired by-product for this reaction [12]. However, in the recent work published on the Du Pont CFB technology [11] it is indicated that the real benefit of operation in the absence of oxygen is that the selectivity can be maintained at higher levels (ca. 10%) but the effect is only observed at conversions >60%, these being important for commercial operation. In this process, the "catalyst" is acting as a stoichiometric oxygen carrier. Recently, the approach has been reported by Du Pont for the ammoxidation of propene and very high selectivity has been reported [13].

Subsequently the use of periodic flow reactors is now attracting increased attention for both gas–gas and gas–liquid reaction systems [14–19]. In this paper we contrast the catalyst performance, in terms of activity and selectivity for non-promoted vanadium phosphates operated in a periodic flow mode in which aerobic and anaerobic conditions can be directly compared for butane oxidation.

2. Experimental

2.1. Catalyst preparation

VPO catalyst was prepared according to the standard route [20]. The VPO precursor was prepared by refluxing V_2O_5 (11.8 g, Aldrich) with H_3PO_4 (16.5 g, 85%, Aldrich) in *iso*butanol (250 ml) for 16 h. The

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light blue solid was recovered by filtration, washed with *iso*butanol (200 mL) and ethanol (150 mL, 100%). The solid was refluxed in water (9 mL H_2O/g solid) for 1 h, filtered hot, and dried in air (110 °C, 16 h). The precursor was then pretreated in a continuous flow reactor (1.5% butane in air) at 400 °C to convert it to the active catalyst. The precursor and the final catalysts were characterised using powder X-ray diffraction (Enraf Nonius FR590 X-ray generator with a $\mathrm{Cu\,K_\alpha}$ source fitted with an Inel CPS120 hemispherical detector) and Raman spectroscopy (Renishaw Ramascope spectrometer fitted with a green Ar^+ laser $\lambda = 514.532$ nm) and the materials were confirmed to be vanadyl hydrogen phosphate hemihydrate and vanadyl pyrophosphate, respectively. The BET surface area of the precursor and final catalyst was the same, 12 $m^2\ g^{-1}$.

VPD catalyst was prepared according to the following standard procedure [20]. The dihydrate $VOPO_4 \cdot 2H_2O$ (4 g, Aldrich) was refluxed with *iso*butanol (80 mL) for 24 h. The pale blue solid was recovered by vacuum filtration and washed with alcohol (50 mL) and acetone (50 mL). The recovered solid was then heated under reflux in water (9 mL H_2O/g solid) for 2 h to remove the impurity $VO(H_2PO_4)_2$. The suspension was then filtered hot, washed with warm water (100 mL) and dried in air (110 °C, 24 h). The precursor was pretreated in a continuous flow reactor (1.5% butane in air) at 400 °C to convert it to the active catalyst. The XRD patterns and Raman spectra confirmed that the precursor was $VOHPO_4 \cdot 0.5H_2O$ and the catalyst was mainly $(VO)_2P_2O_7$. The BET surface areas of the precursor and final catalysts were 18 and 40 $m^2\ g^{-1}$, respectively.

2.2. *Catalyst testing using a periodic flow reactor*

The reactor was fabricated from stainless steel (i.d. = 3.0 mm) and operated at 1 bar pressure, containing catalyst (250–300 μm particles, 0.25 g). Upstream of the reactor a six port sample valve fitted with a 250 μL sample loop was positioned such that the feed gases were fed to the reactor via this valve. Downstream of the reactor tube the gas chromatograph columns were fitted so that the effluent gases from the catalyst bed were continuously fed to the analytical column and thermal conductivity detector (TCD). Under normal operation conditions the reactor containing the catalyst was continuously fed helium as a carrier gas (25 mL min^{-1}). Prior to the start of a reaction the catalyst was heated to the required temperature in a stream of flowing air to ensure the catalyst is fully oxidised at the start of the cycle. Butane in either air (aerobic experiment) or argon (anaerobic) were introduced to the gas sample valve via calibrated mass flow controllers (total flowrate = 50 mL min^{-1}). Samples 250 μL) of this feed were fed to the reactor as discrete pulses using the injection mode of the sample valve. Following each anaerobic experiment a single 250 μL pulse of the reactants was passed over the catalyst and the products were analysed. After 30 min, when the gas chromatographic analysis was completed, a 250 μL pulse of O_2 was passed through the reactor to regenerate the catalyst. At all times the flow of helium through the catalyst bed was maintained. All experiments were conducted several times to ensure reproducible data are reported.

3. Results and discussion

Two sets of experiments were carried out using the non-promoted vanadium phosphate catalysts. First, experiments were carried out using a fixed butane concentration (1.5%) and the temperature increased sequentially from 330 to 400 °C. This butane concentration was selected since it was typical of that used in the standard fuel lean process. Another set of experiments were carried out at 350 °C with butane concentrations in the range 0.9–2.9%. For both sets of experiments eight data sets were obtained at each condition, all of which showed reproducible behaviour as shown in figure 1 for the VPO catalyst, and the performance of aerobic feeds (butane/air) was contrasted with that of the anaerobic feed (butane/argon).

For the catalyst prepared using the VPO method and tested with 1.5% butane, the conversion increased and the selectivity decreased with increasing temperature as expected for these catalysts (table 1). In the absence of co-fed oxygen the conversion was slightly higher as was the selectivity. The effect was most pronounced at the lower temperature, but at the higher conversions required for this reaction in commercial reactors the difference between the two methods of operation was minimal, although an enhancement was still observed. The observation that the presence of oxygen is partially deleterious is consistent with the seminal studies of Contractor and co-workers. In our work, each pulse comprises 1.56×1.0^{-7} mol butane and the reactor contains 8×10^{-4} mol $(VO)_2P_20_7$ and consequently there is more than sufficient oxygen available stoichiometrically from the catalyst. Hence, the increase in conversion observed may be related to the competitive adsorption of butane and oxygen at sites on the surface.

In the second set of experiments the effect of variation in the concentration of butane was investigated for a reaction at 350 °C, a temperature at which significant effects on yield and selectivity were observed in the first experiments (table 1). As the butane concentration is increased (Table 2) the conversion decreases and the beneficial effect of operation in periodic mode is at a maximum for 1.5% butane and at higher concentrations the effect was again minimal. This effect was not suggested in the previous studies

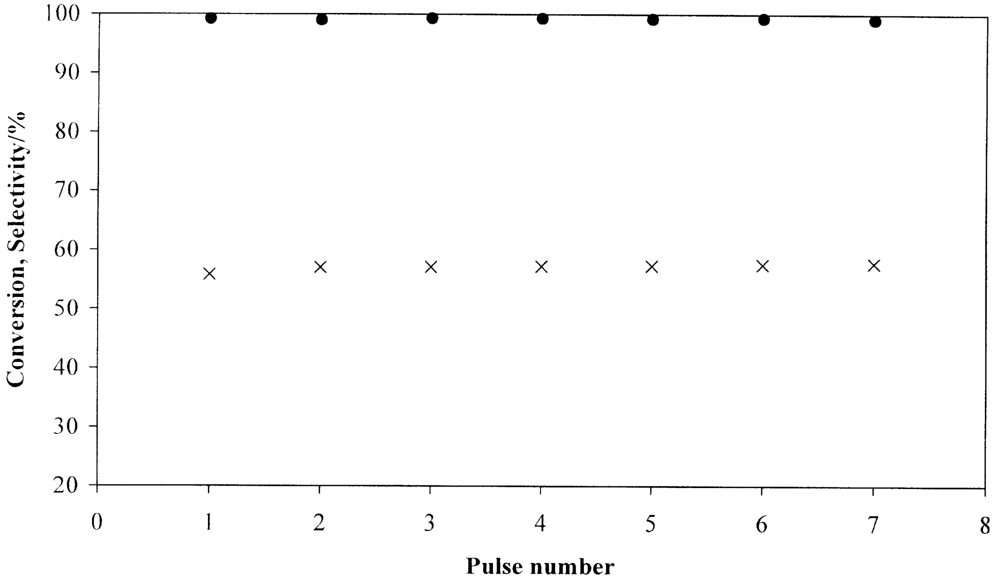

Figure 1. Reproducibility of butane conversion and maleic anhydride selectivity under butane/air periodic flow. (●): Butane conversion, (×): Maleic anhydride selectivity. Conditions: 1.5% butane/air, Sample size in every pulse: 250 μL. Reaction temperature: 400 °C. Catalyst: 0.25 g.

Table 1
Butane oxidation to maleic anhydride over VPO catalyst under gas–gas periodic flow using 1.5% butane/air and 1.5% butane/argon: effect of reaction temperature

T/°C	1.5% butane/air			1.5% butane/Ar followed by O_2			ΔS%*	ΔY%**
	C, %[a]	S_{MA}, %[b]	Y_{MA}, %[c]	C, %	S_{MA}, %	Y_{MA}, %		
330	70.4	69.1	48.6	71.0	75.6	53.6	6.5	5.0
350	86.7	65.2	56.5	88.3	71.4	63.0	6.2	6.5
380	93.2	61.8	57.6	94.4	65.7	62.0	3.9	4.4
400	99.2	57.3	56.8	99.1	58.2	57.7	0.9	0.9

[a] C denotes butane conversion; [b] S_{MA} denotes maleic anhydride selectivity; [c] Y_{MA} denotes maleic anhydride yield.
* ΔS % denotes the selectivity enhancement when operated in butane/Ar mode compared with butane/air mode.
** ΔY % denotes the yield enhancement when operated in butane/Ar mode compared with butane/air mode.

Table 2
Butane oxidation to maleic anhydride over VPO catalyst at 350 °C under gas–gas periodic flow: effect of butane concentration

Butane %	Butane/air			Butane/Ar followed by O_2			ΔS%	ΔY%
	C, %	S_{MA}, %	Y_{MA}, %	C, %	S_{MA}, %	Y_{MA}, %		
0.9	87.8	69.2	60.8	86.6	71.0	61.5	1.8	0.7
1.5	86.7	65.2	56.5	88.3	71.4	63.0	6.2	6.5
2.1	78.2	70.6	55.2	70.4	73.1	51.5	2.5	−3.7
2.9	79.0	70.0	55.3	74.9	72.3	54.2	2.3	−1.1

since the it was indicated that the beneficial effects of anaerobic operation were apparent for butane concentrations between 0.6–50% [11].

Similar sets of experiments were conducted for the VPD material. Using 1.5% butane, lower conversion and selectivity were observed in the absence of co-fed oxygen than those in the presence of oxygen (table 3). More interestingly furan was observed as a product in anaerobic conditions. Similar results were observed when the catalyst was tested at 350 °C with the butane concentrations in the range 0.9–2.9% (table 4). The performance of VPD under periodic flow conditions was in marked contrast to the performance typically observed in a continuous flow microreactor (table 5). Using a feed of 1.5% butane in air at 400 °C in the continuous flow microreactor, the performance of VPO

Table 3

Butane oxidation to maleic anhydride over VPD catalyst under gas–gas periodic flow using 1.5% butane/air and 1.5% butane/argon: effect of reaction temperature

T/°C	1.5% butane/air			1.5% butane/Ar followed by O_2				
	C, %	S_{MA}, %	Y_{MA}, %	C, %	S_{MA}, %	S_{furan}, %[a]	Y_{MA}, %	Y_{furan},%[a]
330	64.7	51.2	33.1	37.6	2.2	8.6	0.8	3.2
350	83.3	35.5	29.6	76.9	11.9	6.8	9.2	5.2
380	99.5	28.2	28.1	99.1	13.5	1.8	13.4	1.8
400	100	24.0	24.0	100	11.4	0.4	11.4	0.4

[a] S_{furan} and Y_{furan} denote furan selectivity and yield, respectively.

Table 4

Butane oxidation to maleic anhydride over VPD catalyst at 350 °C under gas–gas periodic flow: effect of butane concentration

Butane %	Butane/air			Butane/Ar followed by O_2				
	C, %	S_{MA}, %	Y_{MA}, %	C, %	S_{MA}, %	S_{furan}, %	Y_{MA}, %	Y_{furan}, %
0.9	98.4	46.6	45.9	83.9	15.4	11.7	12.9	9.8
1.5	83.3	35.5	29.6	76.9	11.9	6.8	9.2	5.2
2.1	84.6	46.3	39.2	80.3	12.7	8.9	10.2	7.1
2.9	61.3	59.6	36.5	33.0	15.4	11.5	5.1	3.8

Table 5

Butane oxidation to maleic anhydride over VPO and VPD under continuous flow condition using 1.5% butane/air*

Catalyst	380 °C		400 °C	
	C, %	S_{MA}, %	C, %	S_{MA}, %
VPO	19.8	63.8	29.9	61.4
VPD	45.2	67.2	60.4	63.5

* Catalyst testing conditions: 0.25 g catalyst (250–355 μm). 1.5% butane/air, flowrate: 15 mL min^{-1}.

and VPD is governed by the surface area of the catalysts and the selectivities to maleic anhydride are very similar. It is clear that the availability of the selective oxygen species is readily established for both VPO and VPD under continuous flow conditions. With the VPO material, this is maintained for periodic flow but, interestingly, VPD becomes much less active under periodic flow. We plan detailed temporal analysis of products (TAP) experiments to explain this effect further.

4. Conclusions

The results of this study indicate that the benefit of operation in anaerobic conditions depends strongly on the nature of the vanadium phosphate catalyst. For a standard VPO catalyst this benefit is not particularly marked and the small positive effects would not offset the complexity of the process when operated at a commercial level. However, positive effects from periodic flow operation are observed with this material, which has a preparation method and formulation that is similar to industrial standard catalysts. For the VPD material, pronounced differences were observed using the periodic flow reactor under anaerobic conditions when compared with aerobic conditions. The formation of maleic anhydride was markedly decreased and furan was observed, but mainly the formation of carbon oxides was enhanced. In contrast to the steady state operation in a flow reactor, the VPD material was, therefore, a much poorer catalyst in periodic flow operation, particularly in contrast to the VPO material.

Acknowledgements

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