

SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE UNDER OXYGEN-DEFICIENT CONDITIONS OVER V-P-O MIXED OXIDES

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ABSTRACT

The selective oxidation of n-butane to maleic anhydride over V-P-O mixed oxides was studied under oxygen deficient conditions. The mixed oxides were prepared with P/V atomic ratios ranging from 0.7 to 1.0. Catalysts with P/V < 1.0 did not show any selectivity to maleic anhydride formation, regardless of whether or not $(VO)_2P_2O_7$ was present. For catalysts with P/V = 1.0, containing $(VO)_2P_2O_7$ and/or the so-called β^* -phase, the selectivity was strongly influenced by the actual surface V^{5+}/V^{4+} ratio. This ratio is determined by the temperature, the crystal phases present in the catalyst and the composition of the gas mixture. Optimal selectivity was obtained at 425°C with 15% butane in air and a butane/oxygen ratio of 0.9.

INTRODUCTION

Benzene has for many years been the most important feedstock for the production of maleic anhydride (MA). The search for a more economical feedstock was initiated by the rapid increase in benzene prices caused by the increase in oil prices and to the increased use of aromatics in unleaded automobile fuels, this trend being stimulated by tighter benzene-emission control standards. Thus the benzene process has been replaced gradually in the last ten years by the selective oxidation of n-butane (or butylene). The catalysts used are mostly V-P-O mixed oxides, materials which are known to be active and selective for this oxidation reaction [1,2].

The relationship between the methods of preparation, the catalyst structure and the selectivity for MA production has been reviewed recently by Hodnett [3]. For the active catalysts the P/V atomic ratio is typically in the range 1.0-1.2 and the average vanadium oxidation state is in the range 4.1-4.3. It appears, in spite of much research effort, that the efficiency of n-butane-based plants is still only 60-70% of that of benzene-based plants. Commercial butane-based plants work with a gas-mixture of 1.5% butane in air and have a maximum yield of 50-60% at a conversion of 90-100%.

Attempts have been made to prepare catalysts with higher surface areas than the conventionally used catalysts by preparing the precursor from non-aqueous solutions [4,5] in order to attain higher conversions at lower temperatures [6]

or higher n-butane concentration [7] and hence to improve MA-selectivity. An alternative approach to the achievement of higher selectivity could be to increase the butane concentration to work above the explosion limits rather than below. Only a few patents are concerned with the operation under those conditions [8,9]. It therefore appears to be interesting to look at the possibilities of oxidizing n-butane to maleic anhydride under oxygen deficient conditions, especially when using relative high surface area catalysts. If the yield and selectivity can be improved, it may be possible to make the process based on n-butane more attractive and cheaper than in existing commercial plants.

In this study, catalysts have been prepared by standard techniques. The influence of catalyst structure has been investigated and attention has been paid to the influence of the pretreatment of the catalyst and the surface concentration of V^{5+} . The concentrations of n-butane and oxygen have been varied in order to optimize the yield and selectivity for maleic-anhydride production. The results are compared with the existing state of knowledge of the kinetics and mechanism as investigated by others [6,10,11].

EXPERIMENTAL

Preparation of V-P-O mixed oxides

There are two important ways to prepare vanadium-phosphorus mixed oxides. The first method consists of adding a 5^+ -valent vanadium compound (i.e. V_2O_5) to a refluxing solution containing the phosphorus component and a reducing agent. The vanadium is then reduced and the precipitate which is formed is filtered and calcined [3]. A second method consists of reducing a V^{5+} -compound (e.g. V_2O_5 or NH_4VO_3) with an acid such as HCl, tartaric acid or fumaric acid [12-17]. After reduction, formation of the V-P-O mixed oxide is achieved by adding ortho-phosphoric acid.

We adopted the latter method as modified by Katsumoto and Marquis [5]. This method is based on reduction of the vanadium with an organic medium, as described in the following paragraphs. This method produces catalysts with a relatively large surface area.

Precursor 1. 20 g of V_2O_5 was added to a mixture of 100 ml of isopropanol and 50 ml of benzyl-alcohol and the suspension was refluxed at $110^\circ C$ for 4 hours, this brings about reduction of the vanadium. The solution was then cooled to room temperature and 12.5 g of o-phosphoric acid (85%) was added. The suspension was then refluxed for another 3 hours at $105^\circ C$ in a flow of nitrogen above the mixture. The suspension was filtered and dried for ten hours at $140^\circ C$.

Precursor 2. The same method was used but now using 45 g V_2O_5 , 20 g H_3PO_4 , 200 ml isopropanol and 100 ml benzyl-alcohol.

Precursor 3. As for precursors 1 and 2 with the following amounts: 20 g V_2O_5 , 20 g H_3PO_4 , 100 ml iso-propanol and 50 ml of benzyl-alcohol. All

three precursors were treated in nitrogen, air or a butane/air mixture at the temperatures specified in Table 1. The final temperature listed was established for the time given, after heating from room temperature at a heating-rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$.

Physical characterization of the catalysts

The different phases in the catalysts were determined using XRD-measurements. The identification of the phases was based on literature data [3,12,18]. In some cases, the proportions of $\beta\text{-VOPO}_4$ were estimated from the heights of the relevant XRD-peaks. Standards were prepared by mixing the pure components.

The concentration of vanadium was determined by titration with potassium permanganate, while that of phosphorus was determined either by measuring the PO_4^- -ions by means of ion chromatography or by XRF-measurements. BET-surface areas were measured by argon adsorption at 77K [19].

Catalytic characterization

The pyrex reactor, of a conventional plug-flow type, was placed in a tubular oven. The internal reactor diameter was 0.4 cm. Most of the experiments were carried out with 200 mg of catalyst particles ($0.3 < d < 0.6$ mm), diluted with the same amount of quartz to avoid the formation of hot spots in the bed. The temperature in the bed was measured with a chromel-alumel thermocouple. A mixture of n-butane and air was created by mixing these components with two mass-flow controllers. An optional inert stream (helium) could be added to dilute this gas mixture. The total feed rate in the bed could be varied between 5 and $50 \text{ ml}\cdot\text{min}^{-1}$.

Analysis was carried out with gas chromatography. The oxidized products (maleic anhydride and other by-products such as crotonaldehyde and furan) were analyzed by a gas-chromatograph equipped with flame-ionization-detection using a Poropak-Q column ($L = 2$ m, $D = 1/8$ inch) held at 170°C . The C_4 -isomers and carbon oxides were detected with the same chromatograph but now using thermal conductivity detection and a n-octane column ($L = 2$ m, $D = 1/8$ inch) held at 50°C . All connecting tubing was kept at 150°C to avoid crystallization of the maleic-anhydride.

By measuring the catalytic activity using various particle sizes and flow rates the influence of heat and mass transport limitations was found to be negligible. The pyrex reactor did not contribute to the oxidation activity in the temperature range investigated ($300\text{-}500^{\circ}\text{C}$).

Unless stated otherwise, the catalytic measurements were carried out with a feed rate of $15 \text{ ml}\cdot\text{min}^{-1}$; the gas mixture consisted of 15% butane in air (butane/oxygen ratio 0.9) and the pressure in the reactor was 1.03 bar.

We also prepared V-P-O mixed oxides supported on titania and on γ -alumina.

A mixture of 15% n-butane in air was not oxidized selectively on these samples, in agreement with results reported by Busca et al. [20] for the oxidation of 0.6% n-butane in air. These experiments are therefore not described in detail.

Estimation of the valence state of the surface vanadia

Preliminary experiments were carried out to try to estimate the V^{5+}/V^{4+} -ratio in the surface layer of the catalysts. The rectangular pulse technique proposed by Myamoto et al. [21] as modified by Bosch et al. [22] was applied. Pulses of NH_3+NO were used to reduce surface $V=O$ groups according to the equation:



The production of N_2 in this reaction is related to the number of $V=O$ surface groups reduced. After a fast initial reaction, a stationary situation between V^{5+} and V^{4+} is reached. The initial production of N_2 is thus related to the initial number of surface $V=O$ groups and the production of N_2 in the stationary state to the number of V^{5+} species remaining on the surface. It is assumed that the relative reducibility of the catalysts in the NO/NH_3 system reflects the V^{5+}/V^{4+} ratio on the surface in the presence of butane/air mixtures.

RESULTS

Catalyst structures

The heat treatments of the three precursors and the compounds present in the catalysts as detected by XRD after these treatments are given in Table 1. This table shows clearly the influence of the P/V-ratio and the treatment of the precursor on the formation of the different phases. The catalysts prepared by these treatments were tested with regard to their activity and selectivity for the oxidation of n-butane to maleic anhydride. The temperature was varied between 300°C and 500°C. Precursor 1, with a P/V ratio = 0.7 and the calcined precursor 2 (P/V = 0.9) form mainly β - $VOPO_4$ together with V_2O_5 . These materials do not possess any selectivity towards MA, CO and CO_2 being the only products formed at 300-500°C. Precursor 2 heated in nitrogen forms β - $VOPO_4$ and vanadyl pyrophosphate, $(VO)_2P_2O_7$, but it too, is not selective for formation of MA. Heating precursor 3 (P/V = 1.0) in nitrogen results in the formation of $(VO)_2P_2O_7$, whereas mild heating in air favours the formation of a poorly crystalline material whose principle d values at 4.67, 4.07, 3.14 and 2.52 Å correspond to those of the so-called β^* -phase identified by Hodnett et al. [16]. This β^* -phase transforms into β - $VOPO_4$ after more severe pretreatment (longer times and/or higher temperatures); compare the data for the range of samples PV30b to PV30e in Table 1. (The changes occurring in the XRD-patterns due to these pretreatments at 400-700°C are the same as those reported by Hodnett and Delmon [17] for a precursor (P/V = 1) calcined at a constant temperature of 500°C

for different times.) Heating in a butane/air mixture at this temperature results mainly in $(VO)_2P_2O_7$, as is the case after heating in nitrogen. This phase also develops after first heating at 420°C in air for 3 hours and then in a 1% n-butane in air mixture [23].

TABLE 1
Treatment of the different precursors

Precursor Code	Treatment	Phases	S_{BET} m^2g^{-1}	Remarks	
1	PV10	air, 500°C, 5h	β -VOPO ₄ +V ₂ O ₅	5	
P/V=0.7	PV1N	N ₂ , 500°C, 5h	β -VOPO ₄ +V ₂ O ₅	-	
2	PV20a	air, 400°C, 2h	β -VOPO ₄ +V ₂ O ₅	10	
P/V=0.9	PV20b	air, 500°C, 5h	β -VOPO ₄ +V ₂ O ₅	6	
	PV20c	air, 500°C, 10h	β -VOPO ₄ +V ₂ O ₅	-	
	PV2Na	N ₂ , 400°C, 2h	β -VOPO ₄	-	
	PV2Nb	N ₂ , 500°C, 1.5h	β -VOPO ₄ +(VO) ₂ P ₂ O ₇	33	
	PV2Nc	N ₂ , 500°C, 5h	β -VOPO ₄ +(VO) ₂ P ₂ O ₇	52	
	PV2Nd	N ₂ , 500°C, 10h	β -VOPO ₄ +(VO) ₂ P ₂ O ₇	40	
3	PV3Na	N ₂ , 400°C, 2h	(VO) ₂ P ₂ O ₇	24	
P/V=1.0	PV3Nb	N ₂ , 500°C, 1.5h	(VO) ₂ P ₂ O ₇	29	
	PV3Nc	N ₂ , 500°C, 5h	(VO) ₂ P ₂ O ₇	23	
	PV3Nd	N ₂ , 500°C, 10h	(VO) ₂ P ₂ O ₇	20	
	PV30a	air, 400°C, 2h	β^* -phase+(VO) ₂ P ₂ O ₇	22	
	PV30b	air, 500°C, 5h	β^* -phase	12	
	PV30c	air, 400°C, 56h	β^* -phase+ β -VOPO ₄	10	5% β -VOPO ₄
	PV30d	air, 500°C, 10h	β^* -phase+ β -VOPO ₄	10	10% β -VOPO ₄
	PV30e	air, 700°C, 2h	β^* -phase+ β -VOPO ₄	7	20% β -VOPO ₄
	PV3B	15% C ₄ in air 500°C, 4h	(VO) ₂ P ₂ O ₇	-	

1,2,3: Number of the precursor

O/N/B: Treatment (O=air, N=nitrogen, B=butane/air)

a/e : Time and temperature of treatment

Catalytic characterization

All the samples given in Table 1 were tested. Catalysts prepared from precursor 1 and 2 gave total oxidation only. It was found that only pure $(VO)_2P_2O_7$ (PV3Na-d) and the catalysts containing the β^* -phase (PV30a-e) had

any selectivity towards MA under our conditions. The main products detected were n-butane, maleic anhydride and carbon oxides. By-products were crotonaldehyde, furan and fractions of other C_2 and C_4 -molecules. Only traces of dehydrogenation products were found. The results for the selective catalysts are given in Figures 1 to 3 and Tables 2 to 4 and these will now be discussed in turn.

TABLE 2
NO-NH₃-pulse characterization at 450°C

Catalyst	β -VOPO ₄	AV	x_i (%)	x_s (%)
PV3Nd		4	0.42	0.22
PV30c	5%	4.05	0.82	0.28
PV30d	10%	4.1	0.83	0.48
PV30e	20%	4.2	0.82	0.82

AV = average vanadium valency

x_i = initial NO conversion

x_s = NO conversion in the stationary state

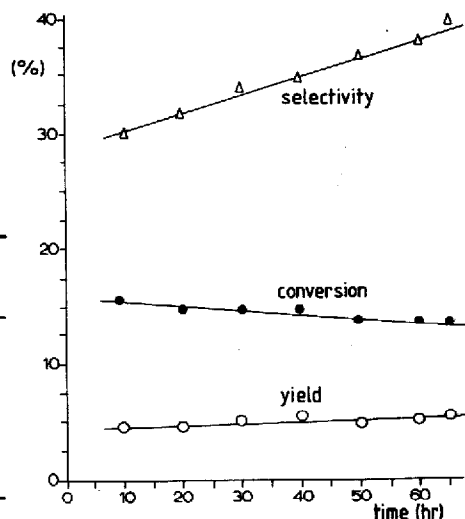


Figure 1 Influence of the time on stream (Precursor 3)

The XRD-pattern of the unreacted precursor 3 was identical with that of a precursor with P/V = 1.01, kindly supplied by Dr. Centi; the latter sample was prepared in an identical fashion. Both spectra consisted mainly of broad peaks. Starting from a non-activated precursor 3, the butane conversion decreased with time while the yield of MA simultaneously increased slightly; a typical example of these changes is shown in Figure 1. The XRD-patterns after catalytic reaction showed mainly sharp peaks of the $(VO)_2P_2O_7$ phase, especially those due to the reflections from the (020)-planes.

A similar experiment was carried out for 65 hours at 425°C with the sample PV3Nd (consisting of $(VO)_2P_2O_7$). Before reaction, but after activation at 500°C for 10h, this catalyst still showed a broad (020)-peak of the $(VO)_2P_2O_7$ phase; the same XRD-pattern was found when the same heat treatment was given to the sample supplied by Dr. Centi. The selectivity of 50% was reached immediately and it remained stable during the whole period on stream. After the catalytic reaction, the $(VO)_2P_2O_7$ phase was still predominant, with a sharp peak for the reflection from the (020)-planes. The sharpening of this peak is likely to be due to the strongly reducing character of the reaction mixture.

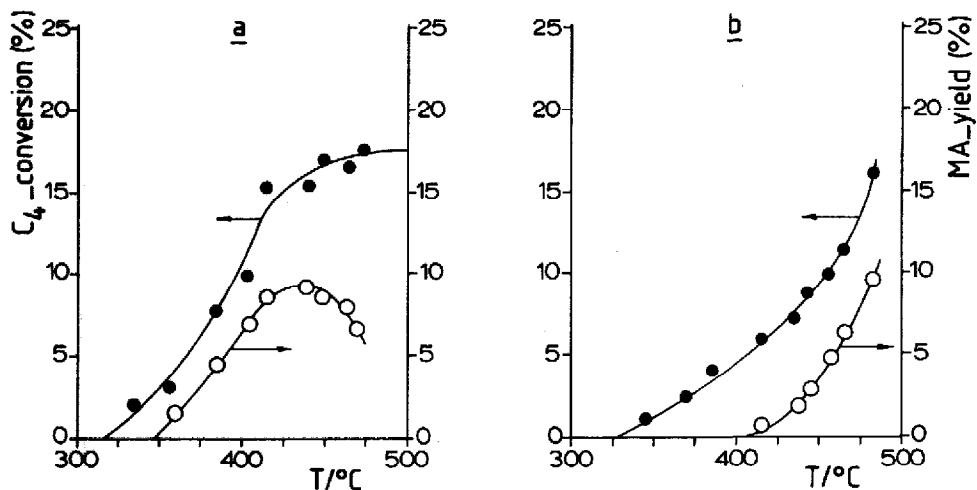


Figure 2 Activity and MA-yield as a function of temperature. SV = 47 min⁻¹; 15% butane, butane/oxygen = 0.9

a PV3B: (VO)₂P₂O₇

b PV30c: β* + 5% β-VOPO₄

TABLE 3

Influence of the butane/oxygen-ratio at 450°C on catalyst PV3Nd, SV = 47 min⁻¹

Butane/O ₂	Butane conversion (%)	Yield		MA selectivity (%)
		MA (%)	CO/CO ₂ (%)	
0.7	18.9	7.5	10	39
0.9	16.6	8.2	6.9	49
1.8	12.4	5.4	5	44
3.1	7.3	2.4	3.5	32

TABLE 4

Influence of the partial pressures of butane and oxygen at a constant butane/oxygen ratio 0.9 on the maximum yield of catalyst PV3Nd

P butane (atm)	P oxygen (atm)	Maximum yield (%)	Maximum selectivity (%)
0.16	0.18	9	80
0.08	0.09	4	27
0.04	0.04	2	9
0.01	0.01	nil	nil

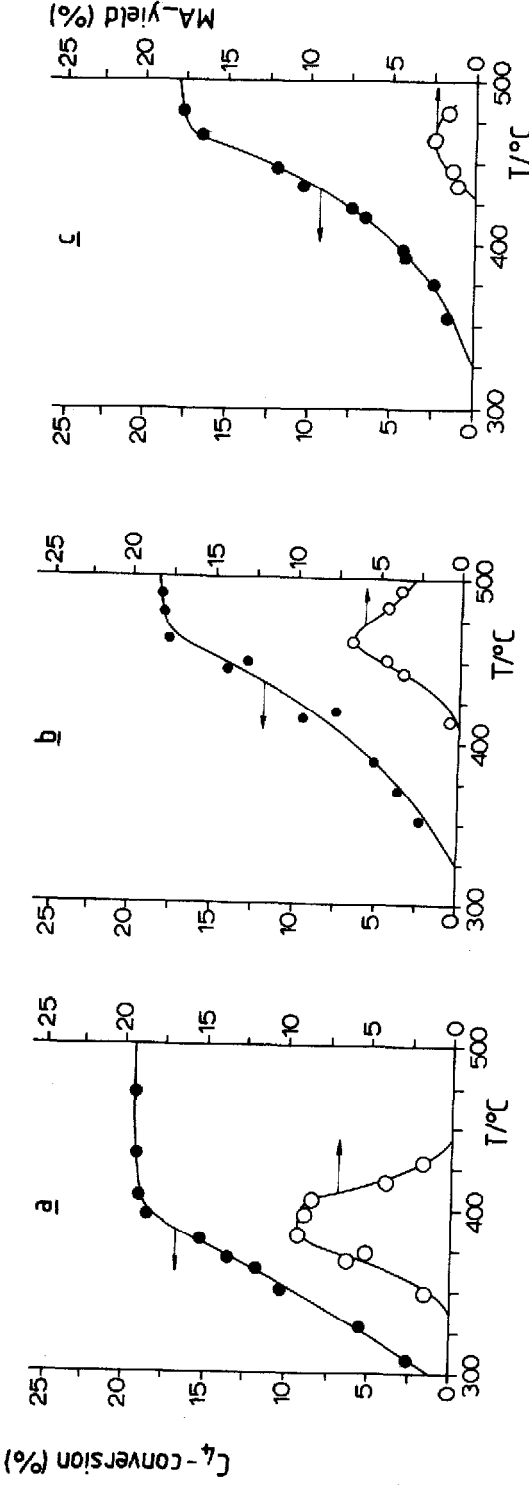


Figure 3 Influence of the structures present in PV3-catalysts; see Figure 2 for experimental conditions
a PV3Nd: $(VO)_2P_2O_7$
b PV30d: $\beta^* + 10\% \beta-VOP_4$
c PV30e: $\beta^* + 20\% \beta-VOP_4$

The relation between catalytic activity and temperature is shown in Figure 2 for the catalyst samples pretreated in a different way, PV3B and PV30c. Pretreatment in the more reducing butane/O₂ mixture (sample PV3B) favours the formation of MA; the maximum yield is obtained at 425°C and the activity and selectivity do not change with time. After pretreatment in air (sample PV30c) a slightly higher yield is obtained at 480°C (Figure 2b). In both cases the XRD-patterns after catalytic reaction again showed mainly sharp peaks of the (VO)₂P₂O₇ phase, especially those due to the reflection of the (020)-planes. This change in crystal structure during reaction is accompanied by changes in activity and selectivity only in the case of a non-activated precursor.

The catalytic performance of the PV3-series was tested in the range 300-500°C, the results being given in Figure 3. The influence of the nature of the phases present on the total activity is not very pronounced in spite of the decreasing BET-surface areas. The average bulk valency (AV) of the vanadium in these catalysts ranges from 4.0 to 4.2; AV is determined from the theoretical valencies in the different structures using the relationship:

$$AV = \{5.[V^{5+}] + 4.[V^{4+}]\} / \{[V^{5+}] + [V^{4+}]\}$$

The way in which the MA-yield changes with reaction temperature is very different for each of the catalysts and there is an optimum temperature for each; when the maximum moves to higher temperatures, the activity is lowered. It could very well be that the average (bulk) vanadium valency does not reflect the actual ratio V^{5+}/V^{4+} on the surface. An attempt was therefore made to estimate the surface V^{5+} concentrations by means of a rectangular pulse technique [21,22]. The results are shown in Table 2. In this, the average vanadium valency AV, calculated from the β -VOPO₄ content, is compared with the initial- and steady-state NO conversions, x_i and x_s respectively. The initial conversion of a freshly calcined catalyst is thought to be determined by the number of surface V=O groups while the steady-state conversion reflects the new V^{5+}/V^{4+} ratio created on the surface due to the reducing character of the reactant gas; a zero steady-state conversion would be the result of complete reduction of all the surface V=O groups. All the air-treated PV30 catalysts show the same initial conversions and will therefore have similar proportions of surface V=O groups, despite their difference in AV. The influence of different β -VOPO₄ contents shows up in the steady-state activities: in the PV30e catalyst, with 20% of β -VOPO₄, the number of surface V=O groups initially present remains virtually the same in the stationary situation, whereas a lower content results in a substantial decrease of surface V=O groups. Heat treatment in nitrogen instead of air (PV3Nd) results in a 50% lower concentration of the initially available surface V=O groups and reduction with NO-NH₃ decreases this amount by a further 50%.

The influence of oxygen and butane partial pressures

The butane/oxygen ratio was varied in order to investigate its influence on the activity and selectivity towards MA of the most selective catalyst PV3Nd (consisting mainly of $(VO)_2P_2O_7$). The results are given in Table 3. Both the total conversion and the yield of CO and CO_2 decrease steadily with a decrease in the amount oxygen available. The yield and selectivity of MA reach a maximum at a butane/ O_2 ratio of about 0.9. The yield of the by-products does not change remarkably.

The influence of varying the partial pressures of butane and oxygen simultaneously at a constant butane/oxygen ratio of 0.9 was investigated on the same catalyst at 300-500°C and the results are given in Table 4. The total feed rate was kept constant at $15 \text{ cm}^3 \cdot \text{min}^{-1}$. From experiments not reported here, it was found that the maximum selectivity at any C_4/O_2 ratio occurred at 425°C; the results in Table 4 therefore refer to this temperature. The results therein show that the butane partial pressure strongly influences the MA selectivity; the maximum MA yield obtainable is directly proportional to the butane content.

DISCUSSION

It is recognized in literature [3] that three important factors influence the selective oxidation of C_4 -hydrocarbons to maleic anhydride over vanadium-phosphorus catalysts: the P/V-ratio of the catalyst, the average valence state of the vanadium in the catalyst, and the structure of the phases present. These three factors are strongly interrelated and depend especially on the method of preparation.

Most results on n-butane oxidation have been obtained in experiments with 1-1.5% butane in air. Hodnett et al. [16] observed an increasing selectivity to maleic anhydride on changing the P/V-ratio from 1 to 1.7, but the total activity decreased concurrently. The maximum yield with a substantial activity was obtained at a P/V-ratio of 1.0. Buchanan and Sundaresan [24] prepared two vanadium phosphate catalysts with P/V = 1.0 and 1.1; they found that the former catalyst was approximately twice as active as the latter but that the selectivities to MA were similar. Cavani et al. [25,26] have also reported that the optimal P/V ratio is close to unity; at lower P/V ratios, the decomposition was enhanced, while at higher P/V ratios the activity decreased and the parallel total oxidation to CO and CO_2 is favoured. Van Geem and Nobel [27], on the other hand, recently studied V-P-O mixed oxides with P/V ratios ranging from 0.34 to 2.4, and reported that the selectivity to maleic anhydride does not at all depend on the P/V ratio, but only on C_4 -conversion. Their catalysts were pre-treated in air at 420°C, then in helium at 480°C and subsequently in 1% n-butane

in air at 480°C. The highest activity was found at P/V = 0.5; no correlation could be found between catalytic activity and the content of the V-P-O phases present. Ai [28] showed that in the case of certain catalysts a marked generation of strong-acid sites occurs at P/V = 1.0 and that the high selectivity of these catalysts is related to these sites. Although our experiments with 15% butane in air do not extend beyond a P/V ratio of 1, they seem to be similar to the results of Hodnett et al. [16] and of Cavani et al. [25,26] as there is a relatively high selectivity to MA for this value. However, the application of higher butane partial pressures sometimes leads to quite different results. n-Butane oxidation is considered to be a structure-sensitive reaction but the experimental results seem to be in conflict. Cavani et al. [23] proposed that disorder along the (020)-planes of vanadyl pyrophosphate enhances the activity for the selective oxidation of 1% n-butane to MA. They did not observe variation in the XRD patterns before and after the catalytic tests. Bergeret et al. [29], however, compared two catalysts using 1.6% n-butane in air and were able to show by means of Radial Electron Distribution (RED) measurements that the better one was composed of well-crystallized vanadyl pyrophosphate, combined with an amorphous V⁵⁺-phase. In the present work with 15% n-butane in air, it was found that reaction brings about a change to higher crystallinity, as detected by the sharpening of the relevant XRD-peaks, but that this does not always affect the catalytic behaviour. The XRD-peaks of pyrophosphate in catalyst PV3B, pretreated in a butane/air mixture, became sharper during the catalytic test. This change in crystallinity was accompanied by a decrease in butane conversion, but there was a simultaneous increase in selectivity to maleic anhydride (Figure 1). Catalyst PV3Nd, also mainly pyrophosphate but prepared by treatment in nitrogen instead of in a butane/air mixture, showed a similar change in crystallinity but the activity and selectivity to MA remained virtually the same.

The active phase for the oxidation of n-butane is vanadyl pyrophosphate [12,16], or a mixture of this with β -VOPO₄ [10]; the reduction route is crucial in determining what phase is formed [6]. Moser and Schrader [30] studied both phases as pure model compounds, β -VOPO₄ also producing MA, albeit at a lower yield. The results presented in Table 1 show clearly that the presence of these phases does not assure MA-formation; compare the catalysts of the series PV2N b-d. Treatment with nitrogen of the samples PV1 and PV2 still results in 5-valent vanadium in the bulk. On the other hand, after treatment with air, large amounts of 4-valent vanadium in the form of (VO)₂P₂O₇ are present in the PV3-series. Subsequent treatment with air results in an increase of the amount of 5-valent vanadium (PV30-series), in agreement with the results of Hodnett and Delmon [17]. Treatment of precursor 3 with butane/air or nitrogen results in almost pure (VO)₂P₂O₇; compare samples PV3B and PV3Nd in Table 1. Centi [23]

found the same structure at a P/V-ratio of 1.05 after calcining at 420°C and subsequent heating in a 1% n-butane/air mixture. Figures 1a and 3a show the temperature dependence of the selectivity of these similar phases. The temperatures at which the maximum selectivities were obtained differ by 50°C.

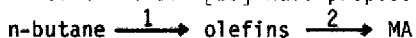
The influence of the butane oxygen-ratio (Table 3) shows an optimal situation for $C_4/O_2 = 0.9$. An increase in C_4 causes a decrease in the yields of MA and carbon oxides and an increase in oxygen favours the production of CO and CO_2 and a concurrent decrease in the yield of MA. As shown in Table 4, a decreasing selectivity to MA is observed with decreasing partial pressures of both butane and oxygen ($C_4/O_2 = 0.9$). Centi et al. [10] assumed that the V^{4+} -sites are responsible for the dehydrogenation of n-butane (redox-couple $V^{4+}-V^{3+}$). Further oxidation should take place on V^{5+} -sites on the surface by means of a $V^{5+}-V^{4+}$ redox couple. The butane and oxygen partial pressures will thus influence the steady-state composition of the catalyst surface, assuming that the structure of a selective oxidation catalyst is such that fast reoxidation of the reduced surface sites by lattice oxygen is impossible [31]. It is assumed frequently that the surface concentration of V^{5+} is related to the amount of 5-valent vanadium in the bulk but this is by no means well established. To explain the extreme difference in selectivity of supported and unsupported catalysts, Busca et al. [20] assumed that n-butane oxidation initially requires a special surface structure. Buchanan and Sundaresen [24] suggested that the surface layer could undergo significant reduction by n-butane and that this was not reflected by the bulk oxidation number.

The surface concentration of V=O groups of some of the catalysts was estimated by means of pulses of NO-NH₃. Table 2 shows that the amount of β -VOPO₄ present does not influence the concentration of surface V=O groups in a fresh catalyst (PV30c-e), whereas the steady-state concentration is roughly proportional to the amount of bulk V^{5+} . The reducing character of C_4/O_2 mixtures will be different from that of a NO/NH₃ mixture, but it is assumed that the reducibility of surface V=O groups by butane/air mixtures will be related to the reducibility by NO-NH₃. Catalyst PV3Nd has already a considerably lower initial amount of surface V=O because of its higher degree of reduction (lower oxidation state) after treatment with nitrogen. The steady state concentration of surface V=O of this catalyst is also lower, and the maximum selectivity is obtained at a temperature which is 50°C lower.

In the work on selective oxidation of butane, no surface V^{5+}/V^{4+} ratios have yet been reported. Some authors were able to determine surface P/V ratios by means of XPS. For example, Hodnett et al. [16] found that these ratios did not change when the bulk ratio ranged from 0.94 to 1.07; for these samples, the selectivity increased from 10 to 50%. Garbassi et al. [18] suggested that the

surface ratios systematically exceeded the bulk values but due to matrix effects, this conclusion was not very clear. However, Garbassi et al. [32] recently confirmed that the surface P/V ratios are higher than would be expected on the basis of the bulk compositions. The NO-NH₃ pulse experiments reported here, however, emphasize the necessity of surface characterization in situ.

Centi et al. [10] have proposed the following reaction scheme:



where step 1 proceeds over reduced surface sites and the subsequent selective oxidation reaction of step 2 over oxidized sites. The NO-NH₃ pulse experiments strongly suggest that many of the conflicting results reported in the literature may be explained by the influence of experimental conditions on the ratio of reduced sites to oxidized sites as well the necessity for proper pretreatment.

The different phases show many differences in selectivity towards MA. At a P/V-ratio below 1.0, the presence of (VO)₂P₂O₇ and β-VOPO₄ (PV2N) does not result in MA formation under our conditions of excess butane. These are the phases responsible for the selective oxidation of butane below the explosion limits [12,13,33]. Under conditions where butane is in excess, the only phase existing is (VO)₂P₂O₇; i.e. there are mainly V⁴⁺-ions present in the bulk. The V⁵⁺-ions necessary for the formation of maleic anhydride [6,10,34,35] must therefore exist predominantly on the surface of the catalyst. The stabilizing influence of phosphorus on the V⁴⁺ ions [12,16,18] probably does not apply at the surface; this is because it is possible that the surface P/V ratio may even exceed bulk values.

An explanation may be given of the experiments with varying partial pressures by considering the oxidation state on the surface of the catalyst. A higher oxygen concentration gives rise to a reaction mixture with a higher oxidation power. The amount of V⁵⁺ on the surface will therefore increase and, above the ratio 0.9, this will lead to a decrease in the selectivity. More C₄ in the mixture means a higher reducing power and the amount of V⁴⁺ will increase. The oxygen deficiency prevents a higher MA-yield. The optimal situation is obtained for a C₄/O₂ ratio of about 0.9. This is in agreement with the competitive adsorption of butane and O₂ on the surface, as proposed by Centi [10].

CONCLUSIONS

1. The selectivity towards MA depends not only on the structure but on the pretreatment of the catalyst, given the structure(s) present.
2. The presence of β-VOPO₄ under oxygen deficient conditions decreases the selectivity to MA.
3. The V⁵⁺/V⁴⁺-ratio on the surface strongly influences the selectivity to MA.
4. The partial pressures of the components in the feed influence the valence

state on the surface. The optimal situation is obtained for a butane/oxygen-ratio of 0.9. (15% butane in air at atmospheric pressure in the reactor).

5. Catalytic characterization of V-P-O mixed oxides must involve in situ measurements of surface V^{5+}/V^{4+} -ratios in order that the influence of structure and pretreatment can be interpreted.

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REFERENCES

- 1 R.L. Bergman and N.W. Frisch, US Patent 3, 293, 268 (1966), assigned to Princeton Chemical Research.
- 2 R.L. Varma and D.N. Saraf, *Ind. Eng. Chem.*, 18 (1979) 7.
- 3 B.K. Hodnett, *Catal. Rev. -Sci. Eng.*, 27 (1985) 373.
- 4 R.A. Schneider, US Patent 3,864,280 (1975), assigned to Chevron Research Company.
- 5 K. Katsumoto and D.M. Marquis, US Patent 4,132,670 (1979), assigned to Chevron Research Company.
- 6 G. Centi, G. Fornasari and F. Trifiro, *I & EC Prod. Res & Dev.*, 24 (1985) 32.
- 7 A.F. Dickason, US Patent 3,899,516 (1975), assigned to Sun Ventures Inc.
- 8 R. Higgins and G.J. Hutchings, US Patent 4,222,945 (1980), assigned to ICI.
- 9 R. Higgins and G.J. Hutchings, US Patent 4,317,777 (1982), assigned to ICI.
- 10 G. Centi, G. Fornasari and F. Trifiro, *J. Catal.*, 89 (1984) 44.
- 11 K. Wohlfahrt and H. Hoffmann, *Chem. Ing. Tech.*, 52 (1980) 811.
- 12 E. Bordes and P. Courtine, *J. Catal.*, 57 (1979) 236.
- 13 M. Nakamura, K. Kawai and Y. Fujiwara, *J. Catal.*, 34 (1974) 345.
- 14 G. Poli, I. Resta, O. Ruggeri and F. Trifiro, *Appl. Catal.*, 1 (1981) 395.
- 15 G. Centi, C. Galassi, I. Manenti, A. Riva and F. Trifiro, *Catalysis III*, (G. Poncelet, P. Grange and P.A. Jacobs, Eds.), Elsevier, Amsterdam, 1983, p. 543.
- 16 B.K. Hodnett, Ph. Permanne and B. Delmon, *Appl. Catal.*, 6 (1983) 231.
- 17 B.K. Hodnett and B. Delmon, *Appl. Catal.*, 9 (1984) 43, 203.
- 18 F. Garbassi, J.C.J. Bart, F. Montino and G. Petrini, *Appl. Catal.*, 16 (1985) 271.
- 19 H. Bosch and A. Peppelenbos, *J. Physics E: Scientific Instr.*, 10 (1977) 605.
- 20 G. Busca, G. Centi and F. Trifiro, *Appl. Catal.*, 25 (1986) 265.
- 21 A. Miyamoto, Y. Yamazaki, M. Inomata and Y. Murakami, *J. Phys. Chem.*, 85 (1981) 2366.
- 22 H. Bosch, F.J.J.G. Janssen, F.M.G. van den Kerkhof, J. Oldenziel, J.G. van Ommen and J.R.H. Ross., *Appl. Catal.*, 25 (1986) 239.
- 23 F. Cavani, G. Centi and F. Trifiro, *J. Chem. Soc., Chem. Commun.* (1985) 492.
- 24 J.S. Buchanan and S. Sundaresan, *Appl. Catal.*, 26 (1986) 211.
- 25 F. Cavani, G. Centi and F. Trifiro, *Appl. Catal.*, 15(1985) 151.
- 26 F. Cavani, G. Centi and F. Trifiro, *Appl. Catal.*, 9 (1984) 191.
- 27 P.C. van Geem and A.P.P. Nobel, "Influence of the P/V ratio on the oxidation of n-butane and trans-2-butene to maleic anhydride over phosphorous vanadium oxide catalysts", *New Developments in Selective Oxidation*, Louvain-la-Neuve, march 17-18, 1986.
- 28 M. Ai, *J. Catal.*, 100 (1986) 336.
- 29 G. Bergeret, M. David, J.P. Broyer and J.C. Volta, "A contribution to the knowledge of the active sites of VPO catalysts for butane oxidation to maleic anhydride", *New Developments in Selective Oxidation*, Louvain-la-Neuve, march 17-18, 1986.

- 30 T.P. Moser and G.L. Schrader, *J. Catal.* 92 (1985) 216.
- 31 S. Szakacs, H. Wolf, G. Munk, I. Bertoli, N. Wustneck, B. Lucke and H. Seeboth, "On the mechanism of the selective oxidation of butane and 1-butene on vanadyl phosphates", *New Developments in Selective Oxidation*, Louvain-la-Neuve, march 17-18, 1986.
- 32 F. Garbassi, J.C.J. Bart, R. Tassinari, G. Vlaic and P. Lagarde, *J. Catal.*, 98 (1986) 317.
- 33 L. Morselli, F. Trifiro and L. Urban, *J. Catal.*, 75 (1982) 112.
- 34 D. Brkic and F. Trifiro, *I & EC, Prod. Res. & Dev.*, 18 (1979) 333.
- 35 F. Cavani, G. Centi, I. Manenti and F. Trifiro, *I & EC Prod. Res. & Dev.*, 24 (1985) 221.