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Study of the Interaction of 1-Butene with V_2O_5 and Mixed Vanadium and Phosphorus Oxides by Means of Temperature-Programmed Desorption

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The interaction of 1-butene with V_2O_5 and V–P mixed oxides has been investigated by the temperature-programmed desorption (TPD) technique. In V_2O_5 and β-$VOPO_4$ four different types of center have been identified which desorb 1-butene as 2-butenes, furan, acetic acid, and maleic anhydride, respectively. In the case of $(VO)_2P_2O_7$, four types of center have been identified which desorb 1-butene as 2-butenes, furan, acetic acid, and crotonaldehyde. With a mixture of $(VO)_2P_2O_7$ and amorphous V(V) phosphate, these types of center were absent. On the basis of a comparison between the TPD data and those obtained from 1-butene oxidation both in the presence and in the absence of oxygen, it is proposed that $(VO)_2P_2O_7$ and β-$VOPO_4$ are responsible for allylic oxidation and maleic anhydride formation, respectively.

INTRODUCTION

As an alternative to industrial production of maleic anhydride (MA) by the oxidation of benzene, catalysts have been designed in the last few years which enable the product to be obtained from butenes (*1–9*). These processes, however, do not show very high selectivities and there is a large number of by-products which create technical and economic difficulties and higher costs at the separation stage.

This research aims to contribute to improving the catalytic system for oxidation of 1-butene on V_2O_5 and V–P mixed oxides by trying to clarify the mechanism of the reaction. The technique employed is that of temperature-programmed desorption (TPD) (*10, 11*) in association with catalysis using a pulse microreactor.

Features which are not clear from earlier work are the respective parts played by vanadium and by phosphorus, the roles of lattice and adsorbed oxygen, and the type of bond which 1-butene makes with the active centers (*2, 6, 7, 12–14*).

The study of the interaction of 1-butene with the catalysts in the presence and in the absence of oxygen, in a pulse microreactor, and the thermodesorption (TPD) of 1-butene with subsequent GC analysis are intended to supply information on the questions set out above. The present research was carried out on V_2O_5, on β-$VOPO_4$ (*3, 7*), and on mixed oxides of V and P containing $(VO)_2P_2O_7$ either in the pure state or in mixture with V(V) phosphates which have shown high activity and selectivity in catalytic tests in the oxidation of 1-butene into maleic anhydride in flow reactors (*1, 6, 7, 16*).

EXPERIMENTAL

Preparation of Catalysts

Vanadium–phosphorus oxide catalysts designated P/V 1.0a, P/V 1.2a, and P/V 1.4a, where the number signifies the P/V ratio, were prepared by dissolving 26.88 g of V_2O_5 in 250 ml of 37% HCl in a three-way round-bottomed flask equipped with a variable-speed stirrer, a condenser, and a thermoregulated bath. After boiling for 1 h with the condenser under total reflux a quantity of 85% H_3PO_4 was added so as to give the desired P/V ratio. The solution was boiled for 1 h with total reflux and then left to evaporate in an open dish. The resi-

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due was later dried in an oven at 100°C for 3 h and directly calcined for 1 h at 400°C and for 2 h at 500°C.

A sample of pure V_2O_5 was prepared in a similar manner without, of course, the addition of H_3PO_4.

A catalyst designated P/V 1.2b was precipitated in the same way as P/V 1.2a above but slowly calcined from 20 to 400°C (in 1 h) and kept at 400°C for 3 h under vacuum. This second type of procedure led to different compounds as has been reported in a previous paper (*15*).

TPD Measurements

The TPD data were obtained with a Perkin–Elmer F 30 chromatograph. Catalyst, 0.5 g, in the form of 60- to 120-mesh granules was placed in a quartz tube (l = 110 mm, i.d. = 1.6 mm) and introduced into the injector of the gas chromatograph. The catalyst had previously been degassed for 1 h at 400°C in a stream of deoxygenated nitrogen; the same gas was used as transport gas.

The TPD experiments were effected by injecting 0.5 ml of 1-butene respectively at 50, 100, 150, 200, 250, and 300°C by the pulse technique and allowing the residual butene to be evacuated in a stream of nitrogen for 30 min. The temperature of the injector was subsequently raised to 400°C at 30°C/min.

The analysis of the oxidation products was carried out gas chromatographically using a column (l = 100 cm, i.d. = $\frac{1}{8}$ in.) of 80- to 100-mesh Poropak QS. The column was temperature programmed with an initial temperature of 80°C for 2 min, then steps of 10°C/min to 195°C.

For the analysis of 2-butene (*cis* and *trans*) and butadiene, we used a column (l = 200 cm, i.d. = $\frac{1}{8}$ in.) filled with 15% picric acid Carbopack and a temperature programme of an initial temperature of 30°C for 1 min, then steps of 4°C/min to 95°C.

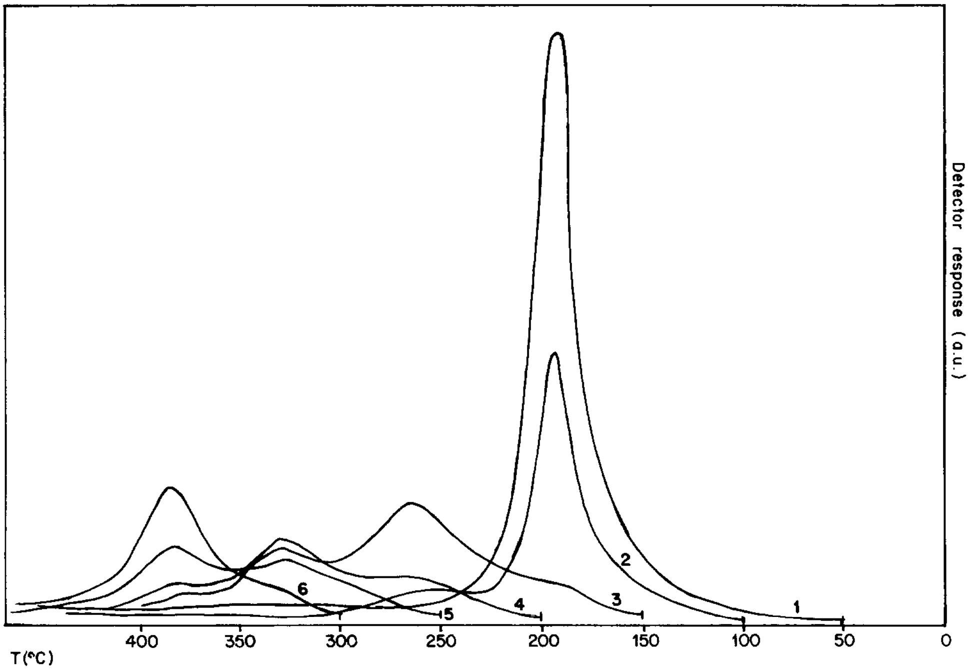

FIG. 1. TPD curves of 1-butene at different temperatures of adsorption on V_2O_5. Adsorption at (1) 50°C, (2) 100°C, (3) 150°C, (4) 200°C, (5) 250°C, (6) 300°C.

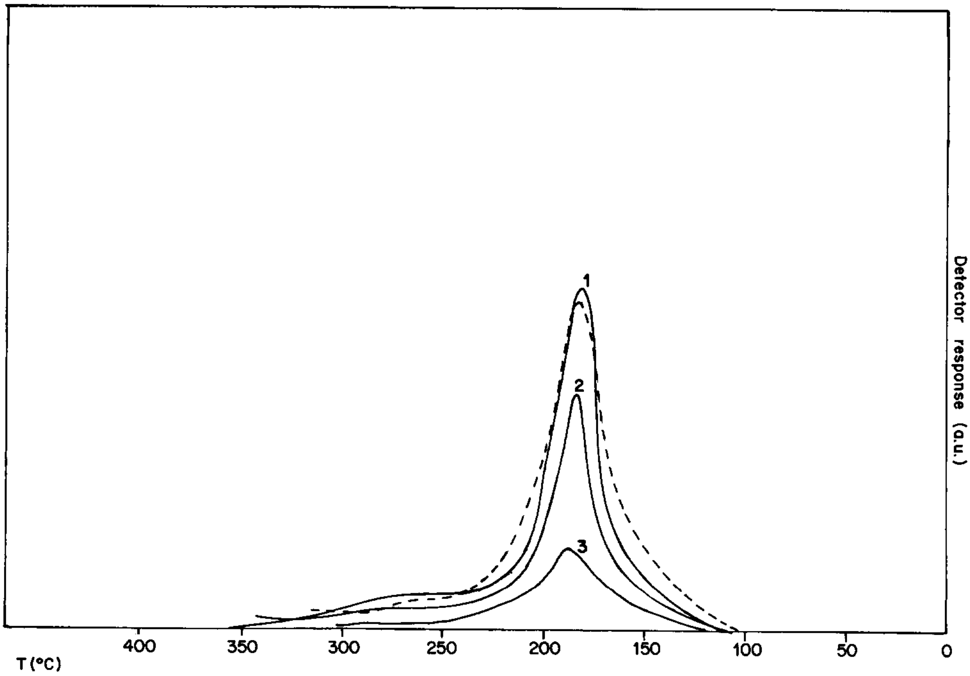

FIG. 2. TPD curves of 1-butene at the same temperature, 100°C, of adsorption on V_2O_5. Solid lines (1,2,3) are successive experiments. Broken line: adsorption at the same temperature of 100°C after treatment with oxygen at 400°C.

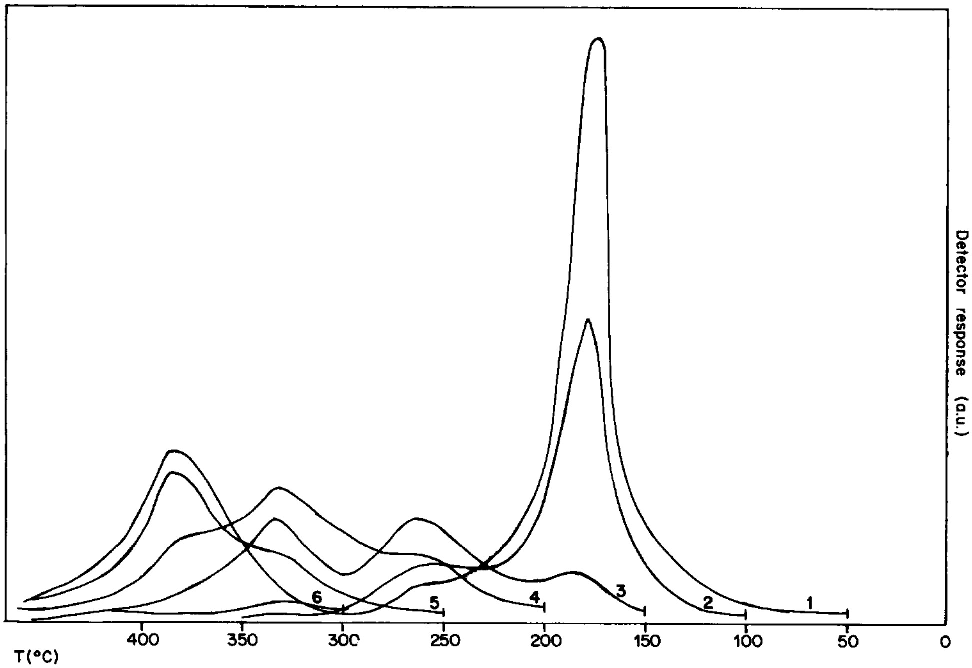

FIG. 3. TPD curves of 1-butene on P/V 1.0a. Adsorption at (1) 50°C, (2) 100°C, (3) 150°C, (4) 200°C, (5) 250°C, (6) 300°C.

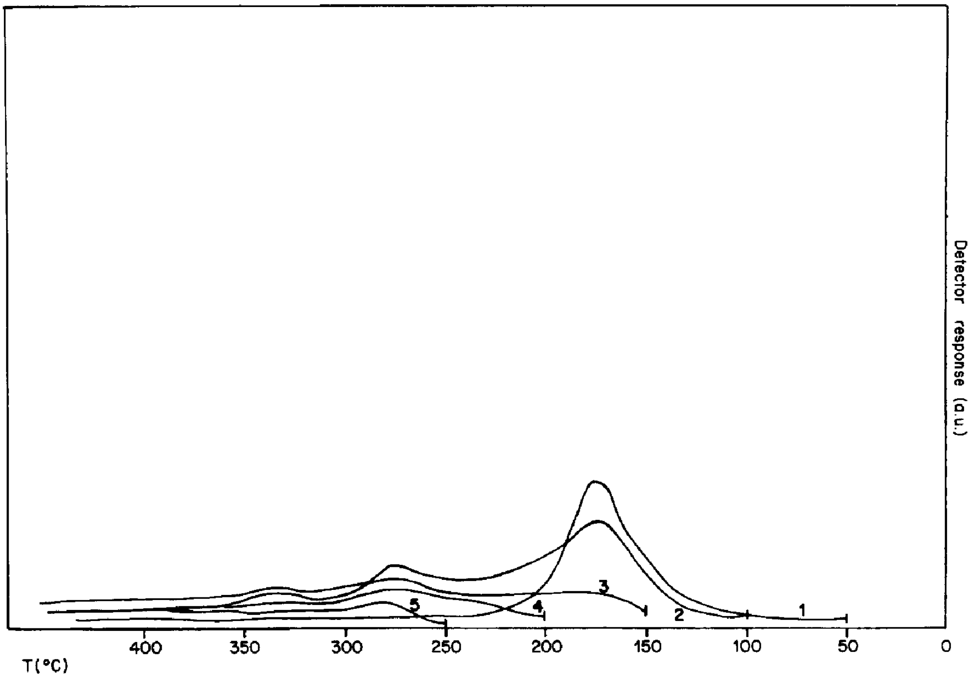

FIG. 4. TPD curves of 1-butene on P/V 1.4a. Adsorption at (1) 50°C, (2) 100°C, (3) 150°C, (4) 200°C, (5) 250°C.

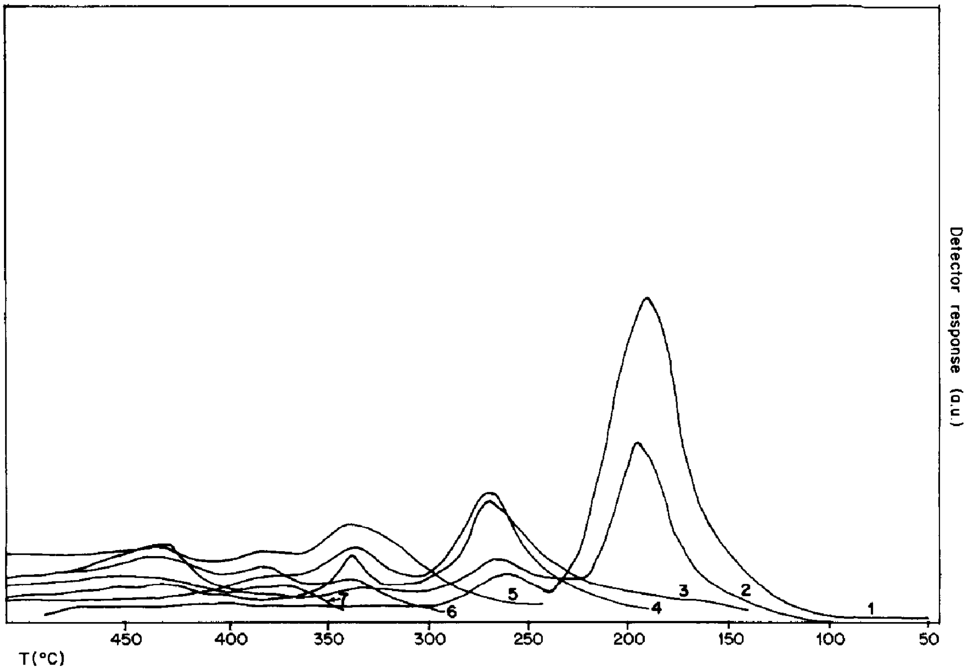

FIG. 5. TPD curves of 1-butene on P/V 1.2b. Adsorption at (1) 50°C, (2) 100°C, (3) 150°C, (4) 200°C, (5) 250°C, (6) 300°C, (7) 350°C.

The TPD curves for the various catalysts are set out in Figs. 1 to 5.

Measurements of Catalytic Activity

Catalytic experiments were carried out on the same apparatus as for TPD measurements by injecting pulses of 1% 1-butene in air or helium at 350°C using the Perkin–Elmer F 30 gas chromatograph equipped with a Poropak QS column. The temperature programme was the same as that used for analysis of the oxidation products.

RESULTS

Chemical Characterization

Table 1 summarizes *d* spacings derived from the X-ray patterns of the different catalysts. In P/V 1.0a and P/V 1.2a the *d* pattern of β-$VOPO_4$ is present. Chemical analysis showed that the percentage of V(V) is 100% as in V_2O_5. In the X-ray pattern of P/V 1.4a the *d* values of $(VO)_2P_2O_7$ are present and the percentage of V(V) was 40%. In P/V 1.2b the *d* values of $(VO)_2P_2O_7$ are present and the percentage of V(IV) was 100%. No change in X-ray pattern was observed after reaction.

TABLE 1

X-Ray *d* Spacings for Catalysts with Various P/V Ratios

V_2O_5	P/V ratio for V–P oxide			
	1.0a	1.2a	1.4a	1.2b
5.6 m	5.20 w	5.22 m	7.07 s	5.7 w
4.36 vs	4.61 w	4.62 m	6.32 w	4.8 w
4.09 w	4.44 w	4.45 vw	4.80 w	3.87 vs
3.40 s	3.57 s	3.57 m	3.86 s	3.14 s
2.88 m	3.48 w	3.48 m	3.13 s	2.98 m
2.76 mw	3.41 m	3.39 s	3.52 vw	2.66 w
2.61 m	3.19 w	3.18 w	2.99 m	2.44 w
1.92 w	3.07 s	3.07 s	2.43 w	
1.75 w	2.21 w	2.82 w		
	1.96 w	2.19 w		

Note. mw = medium weak; vw = very weak; m = medium; ms = medium strong; s = strong; vs = very strong.

TPD Analysis

V_2O_5. Figure 1 shows the TPD curves obtained at different temperatures of adsorption of 1-butene on V_2O_5.

For adsorption at 50°C a single peak of desorption at 180°C (Peak I) was observed. For adsorption at 100°C Peak I is still present, but diminishes in intensity and a new peak appears at 260°C (Peak II).

For adsorption at 150°C Peaks I and II can still be seen and a new peak appears at 320°C (Peak III).

For adsorption at 200°C, the intensity of Peak II diminishes, Peak III is present, and a new peak is formed at 380°C (Peak IV). For adsorption at 250°C Peak II disappears, Peak III is present, and Peak IV increases in intensity.

For adsorption at 300°C Peak III falls further in intensity while Peak IV increases.

Subsequent gas-chromatographic analysis of the single peaks made it possible to identify their nature, namely:

Peak I: 1- and 2-butenes with traces of butadiene;
Peak II: furan;
Peak III: acetic acid and acetic anhydride;
Peak IV: maleic anhydride.

Figure 2 shows the TPD curves in successive tests of adsorption at 100°C and desorption at 400°C: on increasing the number of experiments the peak diminishes, revealing deactivation of the centers responsible for the adsorption. Treating the catalyst with oxygen at 400°C recovers the initial value of the rate of adsorption (broken line). Both the absorption at 600 nm in the diffuse reflectance spectrum and the signal at $g = 1.9$ in the EPR spectrum, which are characteristic of V(IV) species, present before the reoxidation, revealed no appreciable variation on oxygen treatment. The recovery of the adsorption capacity of the solid through the treatment with oxygen may be attributed to an oxidation of possible polymers formed on the surface rather than to the oxidation of the catalyst.

Analysis of the pentoxide after the TPD experiments which followed adsorption of 1-butene at a temperature above 200°C revealed an increase in signal intensity of V(IV) in the EPR spectrum and a large increase in absorption at 600 nm in the diffuse reflectance spectrum, also typical of this species (*14*). The formation of furan, acetic acid, acetic anhydride, and maleic anhydride therefore occurs at the expense of the lattice oxygen of the vanadium oxide.

P/V 1.0a. Figure 3 shows the results of TPD for this catalyst; they are similar to those obtained on V_2O_5 both as regards the temperature of desorption and the number and intensity of peaks and their chemical nature.

The TPD spectra of P/V 1.2a and 1.0a are similar.

P/V 1.4a. This catalyst (Fig. 4) reveals a desorption peak at 180°C much lower in intensity than those obtained on the first two catalysts by adsorption at 50°C, while by adsorption at higher temperature it shows only Peak II. In this case too, Peak I consists of 1- and 2-butene with traces of butadiene and Peak II consists of furan.

P/V 1.2b. This catalyst (Fig. 5) exhibits a desorption peak at 180°C whose area has a value intermediate between that obtained with V_2O_5 and that with P/V 1.4a. It also exhibits Peak II and Peak III, and Peak IV is present also but smaller. In contrast to all other catalysts, P/V 1.2b shows a new peak (Peak V) corresponding to desorption at 420°C and GC analysis revealed the desorbed gas to be essentially crotonaldehyde.

Catalytic Measurements

Oxidation runs in a pulse microreactor. Oxidations of 1-butene were carried out on the catalysts at 350°C in helium and air, respectively. Table 2 gives the conversions and yields of furan, maleic anhydride, and crotonaldehyde. In the case of V_2O_5, the chromatograms obtained with mixtures in the presence of oxygen (i.e., in air) do not show any product of partial oxidation: very probably all the butene is converted into CO and CO_2. The same analysis in the absence of gaseous oxygen showed on the contrary a large number of products of the same nature as those obtained with P/V 1.4a in the presence of air (Fig. 6).

P/V 1.0a and P/V 1.2a behave similarly to V_2O_5.

P/V 1.4a in the presence of air gives high yields of furan and maleic anhydride (Table 2) (Fig. 7), while in the absence of oxygen the conversion diminishes and one obtains mostly butadiene.

TABLE 2

Conversions of 1-Butene at 350°C and Yield in Furan, Maleic Anhydride, and Crotonaldehyde with Catalysts of Different P/V Ratios (Residence Time 0.45 sec)

Catalyst	1-Butene in 1% mixture in helium				1-Butene in 1% mixture in air			
	Conversion (%)	Percentage yield			Conversion (%)	Percentage yield		
		Furan	MA	CA		Furan	MA	CA
V_2O_5	65	—	10	—	78	—	tr	—
1.0a	69	—	9	—	85	—	—	—
1.4a	30	tr	—	—	94	35	21	—
1.2b	25	2	tr	20	80	5	20	4

Note. MA = maleic anhydride; CA = crotonaldehyde; tr = trace.

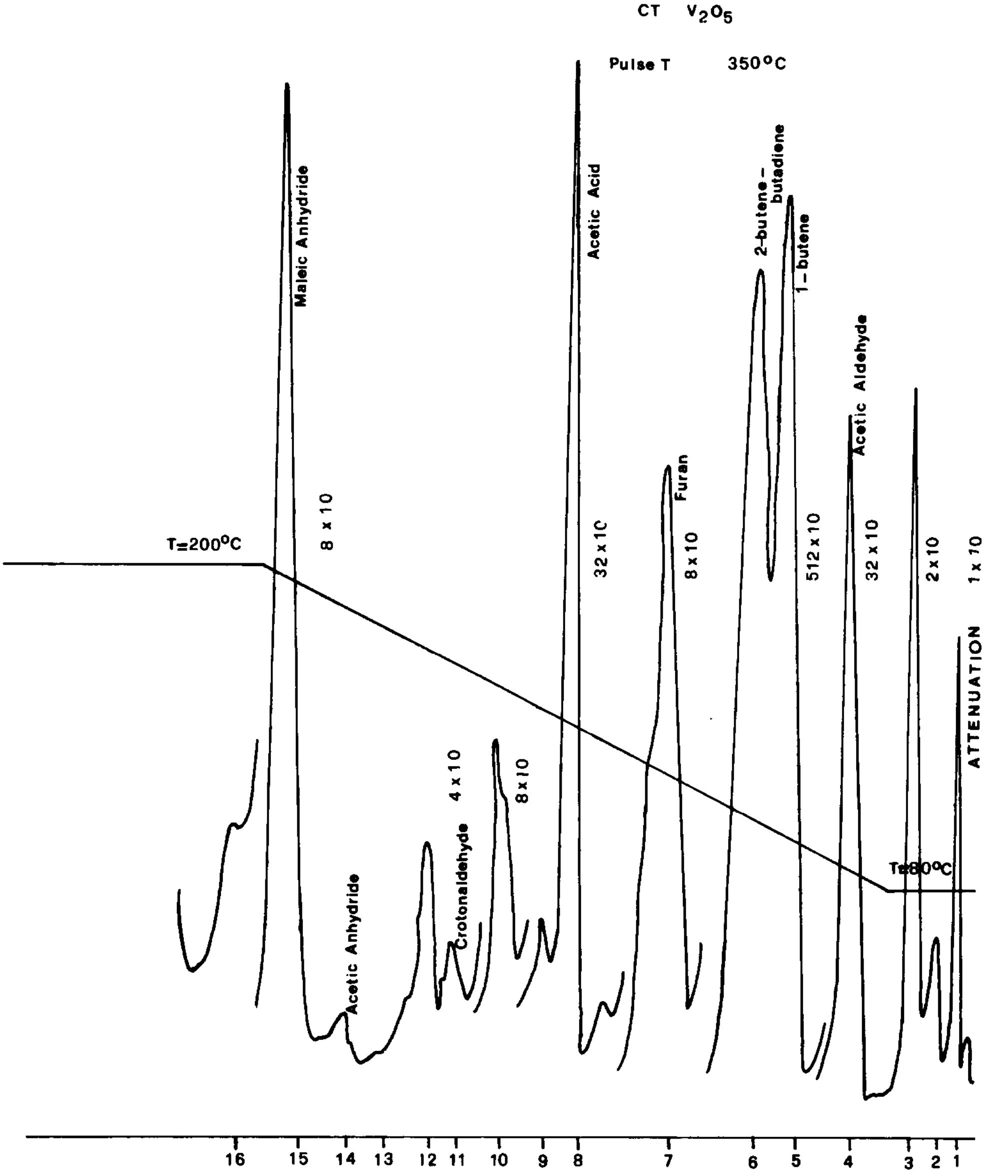

FIG. 6. Gas chromatogram of catalytic activity: V_2O_5 with 1 ml of pure 1-butene.

P/V 1.2b in the presence of air shows high conversion and high yield in maleic anhydride. In the absence of oxygen, the conversion is very low and crotonaldehyde is the main product.

DISCUSSION AND CONCLUSIONS

1-Butene–Surface Interaction

The TPD experiments showed that 1-butene can form five types of bond with the surface of the catalyst.

The five different surface complexes that are formed are characterised by:

(a) different activation energy of formation: the greater the temperature of adsorption necessary in order to have a desorption peak, the greater is the activation energy of formation of the complex;

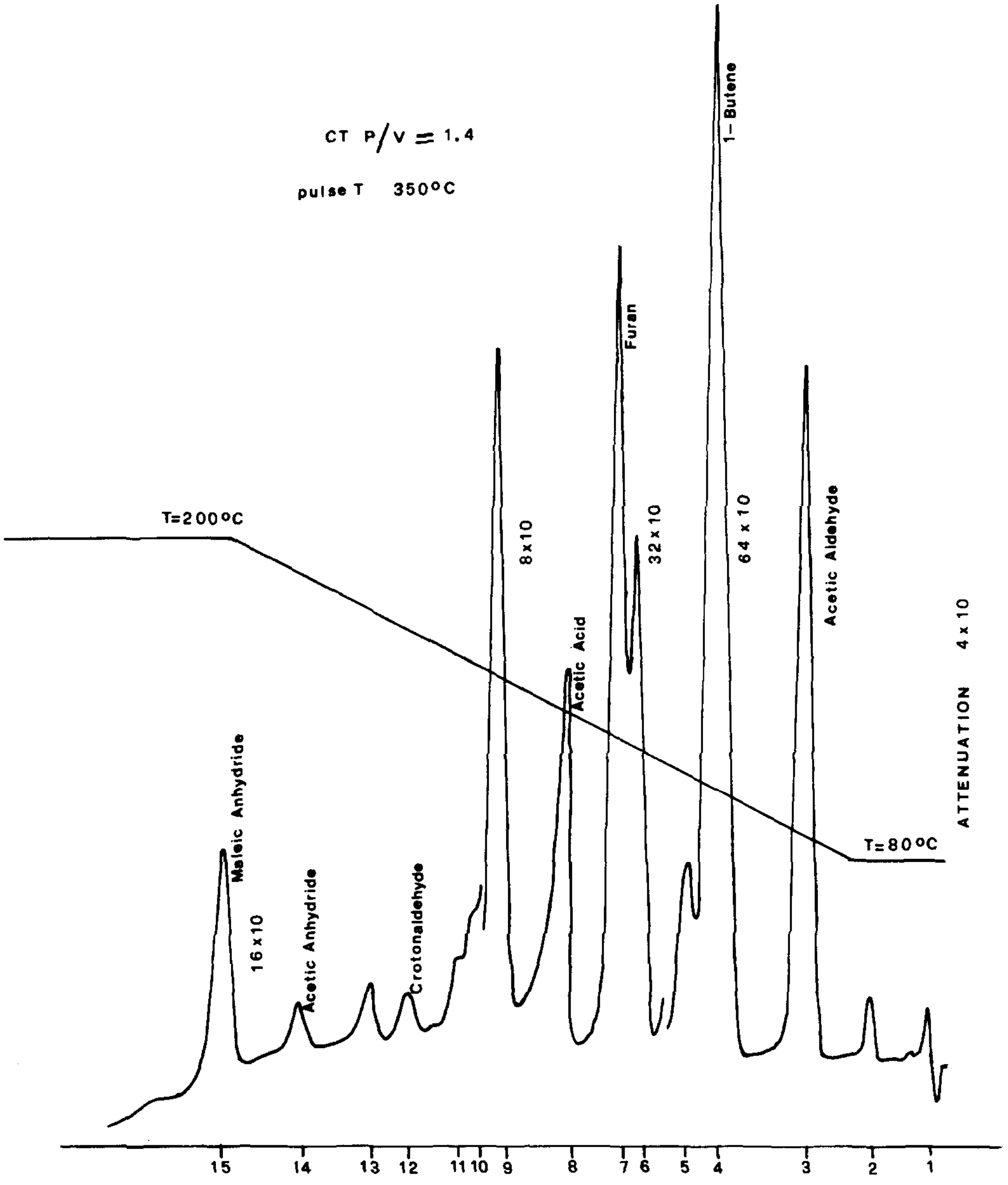

FIG. 7. Gas chromatogram of catalytic activity: P/V 1.4a with mixture of 1-butene/1% air.

(b) different activation energy of decomposition of the surface complex: the greater the maximum temperature of the peak, the greater is the activation energy of desorption which, as an initial approximation, may indicate a greater strength of the surface-complex bond;

(c) different nature of the decomposition product.

Center I

The first center (corresponding to Peak I in TPD) responsible for the isomerization can be an acid center, linked to the presence of OH groups on the surface, which may isomerize 1-butene into 2-butene through an intermediate carbocation or a coordination vacancy in the vanadium which permits adsorption of the olefin with the formation of an intermediate π-allyl.

Center II

This center, linked to Peak II, produces furan. This complex can be formed with bonds between 1- and 2-butene and surface oxygen, or from an interaction with butadiene previously formed. The experiments made with adsorption of butadiene showed in fact two desorption peaks at 260 and 380°C which correspond respectively to furan and maleic anhydride.

Center III

This center, corresponding to Peak III, forms a complex that desorbs as acetic acid and acetic anhydride which might derive from an addition of oxygens to the double bond of 2-butene. Oxyacid addition to olefin double bonds leading to anhydride and acids is well known (*17*).

Center IV

This center corresponds to Peak IV and is linked to a complex that desorbs as maleic anhydride and might be the result of either an interaction between butadiene and surface oxygen or of a successive transformation product of furan.

Center V

This center corresponds to Peak V and is linked to a complex that desorbs 1-butene as crotonaldehyde.

The Role of the Structure

β-$VOPO_4$ behaves both in TPD measurements and in pulse microreactor runs as V_2O_5. These results seem to be in contrast with those reported in the paper of Bordes and Courtine (*7*), where high selectivity in oxidation of 1-butene with β-$VOPO_4$ was found. However, β-$VOPO_4$ is reduced in a flow reactor to $(VO)_2P_2O_7$ (*7*) and therefore activity data obtained in a flow reactor are more related to the reduced phase than to β-$VOPO_4$.

The slight excess of P_2O_5 in P/V 1.2a has no effect either in the pulse microreactor or in TPD experiments, so the excess of H_3PO_4 seems not to contribute to the surface reactivity.

The two catalysts which contain $(VO)_2P_2O_7$ and show respectively 50% of V(IV) and 100% of V(IV) behave in completely different ways from β-$VOPO_4$. P/V 1.4a is a mixture of $(VO)_2P_2O_7$ and an amorphous species containing V(V). In the flow reactor this catalyst was active in butene oxidation but presented a low yield in maleic anhydride (*6*). P/V 1.2b consists of $(VO)_2P_2O_7$ and an excess of H_3PO_4. The role of excess H_3PO_4 was put forward in a previous paper as avoiding the complete oxidation of $(VO)_2P_2O_7$ (*15*). In the flow reactor this catalyst showed a high yield in maleic anhydride comparable to those reported by other authors (*16*).

In the absence of oxygen both the above catalysts are unable to produce maleic anhydride but basically give products of allylic oxidation: P/V 1.2b gives crotonaldehyde, P/V 1.4a gives butadiene. For these two catalysts oxygen is necessary to produce maleic anhydride. The difference in behaviour of the two $(VO)_2P_2O_7$ catalysts can be attributed to the great excess of H_3PO_4 in P/V 1.4a and also to the presence of an amorphous oxidized compound.

From the results reported here it seems that β-$VOPO_4$ is able to produce maleic anhydride and $(VO)_2P_2O_7$ to oxidize 1-butene to butadiene and crotonaldehyde, both known as intermediates (*3*) in the synthesis of maleic anhydride. According to Mount and Raffelson (*1*), the active species must show an X-ray pattern typical of $(VO)_2P_2O_7$ (*1*, *7*), but also a certain percentage of vanadium (V) is claimed. Bordes and Courtine (*7*) suggest the active phase can be a mixture of $(VO)_2P_2O_7$ and another phase.

The data reported in this paper are in agreement with the claims of the patents and the suggestion of Bordes and Courtine, and can be summarized thus:

$(VO)_2P_2O_7$ + 1-butene →
crotonaldehyde and/or butadiene;
β-$VOPO_4$ + 1-butene (butadiene,
crotonaldehyde) → maleic anhydride.

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