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The design of a new ZrO_2-supported V/P/O catalyst for *n*-butane oxidation to maleic anhydride: The build-up of the active phase during thermal treatment

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ABSTRACT

This study concerns the generation of the active V/P/O phase in supported catalysts used for *n*-butane oxidation to maleic anhydride. Catalysts were prepared by impregnating a zirconia support with ammonium vanadate and phosphoric acid, with subsequent thermal treatment under various environments and temperatures. The catalysts were studied by means of *in situ* Raman spectroscopy and reactivity measurements. It was found that the nature of the active surface is greatly affected both by the composition of the gas phase used for the thermal treatment, and by the P/V ratio used for catalyst preparation. δ-$VOPO_4$ was initially formed by the high-temperature reaction of vanadium salt with phosphoric acid; however, in the sample prepared with only 10% excess phosphorus (P/V atomic ratio = 1.1), δ-$VOPO_4$ transformed into either V_2O_5, in a steam-enriched air stream, or α_{II}- and β-$VOPO_4$, in a dry air stream. δ-$VOPO_4$ was more stable in the sample prepared with a large excess of P, i.e., with P/V = 1.3 and 1.5. The latter catalyst showed the best catalytic performance in *n*-butane oxidation. However, the performance was worse than that of the commercial unsupported vanadyl pyrophosphate catalyst.

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1. Introduction

Vanadium/phosphorus mixed oxides are catalysts for gas-phase selective oxidation and ammoxidation of hydrocarbons [1–5]. A great variety of V/P/O compounds exist that differ in terms of oxidation states, degree of phosphate group condensation, and water molecule content. It is also known that the transformation of one V/P/O compound into another can be induced by thermal treatments. The atmosphere at which the treatment is carried out is a powerful tool that can be used to control such transformations [6,7]. The most well known V/P/O system is vanadyl pyrophosphate (VPP), the catalyst used to oxidize *n*-butane to maleic anhydride [1].

V/P/O compounds have a tendency to undergo changes as a consequence of slight variations in either temperature or composition of the atmosphere used for thermal treatments. Therefore, in the past, great attention has been paid to the changes occurring during the thermal treatment of $VOHPO_4{\cdot}0.5H_2O$ (the precursor of VPP) [8] as well as to possible changes that the VPP may undergo under reaction conditions. In previous studies, we found that the surface composition of VPP catalysts is affected by the reaction conditions [9–11]; during reaction a *dynamic equilibrium* is established at the catalyst surface between various V/P/O compounds. However, the nature of the compounds formed on the surface of VPP, that is still the main component of the catalyst, is a function of the P/V ratio adopted for the preparation of this compound. When an excess of P is used with respect to the stoichiometric requirement, under reaction conditions the surface of VPP is oxidized to δ-$VOPO_4$, and the redox cycle occurs between V^{5+} in this latter compound and V^{4+} in VPP; this catalyst gives the optimal performance in *n*-butane oxidation to maleic anhydride. Conversely, when a stoichiometric P/V ratio is used, VPP is oxidized into non-selective α_I-$VOPO_4$ at 340–400 °C which, however, converts into the selective δ-$VOPO_4$ when temperatures higher than 400 °C are used [10,11]. δ-$VOPO_4$ reduces to VPP during reaction, and the amount of the prevailing compound in the active phase is a function of both the reaction conditions and the nature of the rate-determining step [12].

In the present study, we report on the attempt to build-up δ-$VOPO_4$ on the surface of a zirconia-supported V/P/O catalyst. The aim of this approach was twofold: (a) to confirm that δ-$VOPO_4$ is the key-compound for the generation of an active and selective catalyst for *n*-butane oxidation, and that catalyst composition affects the type of V^{5+} phosphate that is formed at high temperature, and (b) to find a method for the preparation of V/P/O-based catalysts in which the dispersion of the latter onto an inert support may lead to a material having lower cost compared to the conventional unsupported VPP. Raman spectra, recorded *in situ* during the thermal treatment, were used together with reactivity measurements to characterize the catalyst surface, with the aim of determining which parameters may influence the generation of the active phase.

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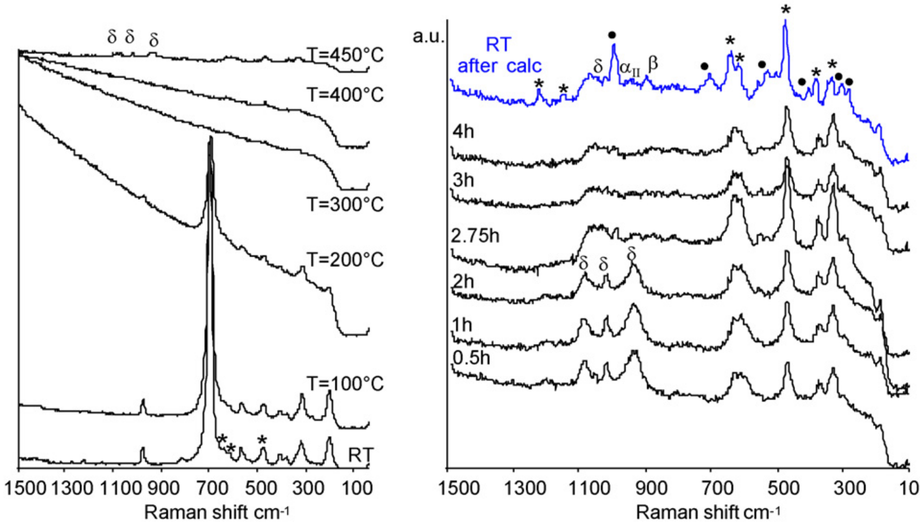


Fig. 1. Raman spectra of the sample prepared by impregnation of zirconia with NH_4VO_3 and H_3PO_4 (P/V atomic ratio 1.1) recorded *in situ* during heating from RT to 450 °C in 14.5% O_2 in a N_2 flow (figure on the left) and then during the isothermal step at 450 °C (figure on the right). Symbols: $\alpha_{II} = \alpha_{II}$-$VOPO_4$; $\beta = \beta$-$VOPO_4$; $\delta = \delta$-$VOPO_4$; • = V_2O_5; * = ZrO_2.

2. Experimental

Catalysts were prepared using the wet impregnation technique: 5.00 g of monoclinic ZrO_2, with a specific surface area of 14 m^2/g, was dropped into an aqueous solution (volume 70 ml) containing 0.38 g of NH_4VO_3 and either 0.41 or 0.48 or 0.56 g (P/V atomic ratio 1.10, 1.30 and 1.50, respectively) H_3PO_4 (85 wt%) (both chemicals supplied by Sigma–Aldrich). The amounts used made it possible to obtain the 10 wt% active phase (calculated by hypothesizing the formation of $(VO)_2P_2O_7$) with respect to ZrO_2. Water was evaporated under slight vacuum at 70 °C. The thermal treatment of samples was carried out either in muffle, or in the cell of the Raman spectrometer.

Catalysts were characterized by means of laser Raman spectroscopy (Renishaw 1000, laser source Argon ion 514 nm, equipped with a Leica DMLM microscope and a commercial cell, Linkam Instruments TS1500 for *in situ* measurements), and X-ray diffraction (Philips PW 1710 apparatus, with Cu Kα, $\lambda = 1.5406$ Å, as the radiation source).

Catalyst surface acidity was measured by FT-IR spectroscopy, by means of a PerkinElmer 1750 Spectrometer. Self-supporting wafers of pure sample were first evacuated at 450 °C *in vacuo* (residual $p = 10^{-6}$ mbar). Then adsorption of pyridine was done at room temperature, and desorption was carried out by outgassing the sample at increasing temperatures. The FT-IR spectrum was recorded after evacuation at each temperature level. The concentration of Lewis and Brønsted acid sites was calculated using the method proposed by Eines [13] (extinction coefficient for Lewis sites 2.22, for Brønsted sites 1.67).

Catalytic tests were carried out in a quartz continuous-flow reactor, loading 0.8 g of catalyst (W/F = 1.3 g s ml^{-1}) and feeding 1.7% n-butane and 17% oxygen (remainder N_2). Products were analyzed *on-line* by means of a gas chromatograph equipped with a HP-1 column for the separation of unconverted *n*-butane, maleic anhydride and light by-products: formaldehyde, acrylic acid, acetic acid, crotonaldehyde. A Carbosieve SII column was used for the analysis of oxygen, CO and CO_2. The gaseous effluent stream was also bubbled for 2 h either in acetone (this fraction was then analyzed by means of GC) or in water, for the identification of the heavy compounds (mainly phthalic acid, benzoic acid, and methyltetrahydrobenzoic acid). The aqueous solution was analyzed by means of HPLC–MS, using a Lichrosorb RP18 200 mm × 4.6 mm 10 μ column (eluents formic acid and acetonitrile). Maleic acid was determined by titration with NaOH 0.1N, after subtraction of the contribution deriving from the other acids formed.

3. Results

3.1. Characterization of samples

Fig. 1 shows the Raman spectra recorded *in situ* during the heating of the dried P/V 1.1 sample in 14.8% O_2 in N_2 flow (figure on the left) and during the isothermal step at 450 °C (figure on the right). The spectrum of the RT sample shows bands that are attributable to the zirconia support (at Raman shift 180, 340, 380, 474, 535, 555, 615, 636, 1145 and 1220 cm^{-1}), and bands at 700 cm^{-1} (very strong), 204, 318 and 976 cm^{-1}; these latter bands are not attributable to ammonium vanadate or to any other V compounds. It is worth noting that the solid obtained by reacting ammonium vanadate with phosphoric acid in aqueous medium, which yielded $NH_4(VO_2)_2PO_4$ after water evaporation, showed a Raman spectrum that did not correspond to that shown in Fig. 1. This suggests that already during the drying step a reaction occurs between the deposited compounds and zirconia, with the formation of a mixed V/P/Zr/O precursor spread over the zirconia.

During heating, however, all the bands progressively disappeared, and at 300 and 400 °C the spectra did not show any significant bands, not even those attributable to the support. When the temperature was raised above 400 °C, bands attributable to δ-$VOPO_4$ (1090, 1075, 1020 and 936 cm^{-1}) [14,15] and zirconia developed, which then became well evident during the isothermal step at 450 °C. However, a further prolongation of the isothermal step led to the partial transformation of δ-$VOPO_4$ into β- (968 and 892 cm^{-1}) and α_{II}-$VOPO_4$ (945 and 933 cm^{-1}). The spectrum recorded at RT also showed bands attributable to V_2O_5 (998, 705, 483, 305 and 285 cm^{-1}). A similar behavior was shown when the thermal treatment was carried out in a wet (3% steam, 14.5 O_2, remainder N_2) stream (Fig. 2). Also in this case, after 2 h at 450 °C, bands attributable to δ-$VOPO_4$ that formed during the heating step, disappeared; in this case, the compound converted mainly into V_2O_5. Therefore, the presence of steam favored the hydrolysis of $VOPO_4$. In the spectrum recorded at RT, broad bands were visible at around 870–880 and 810–815 cm^{-1}; these bands are attributable

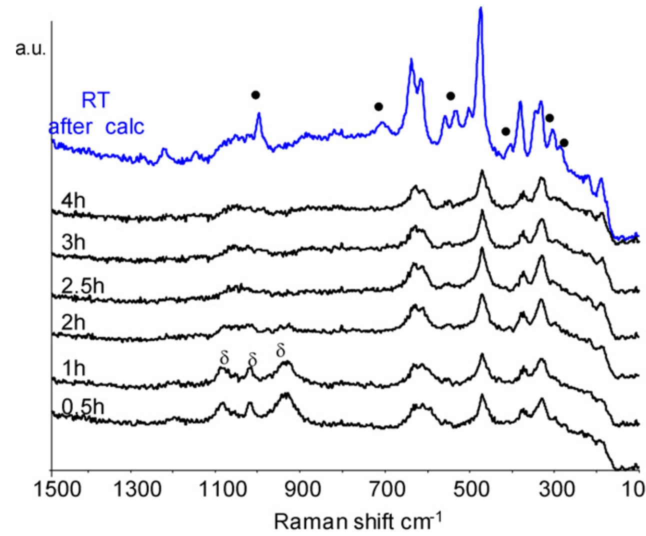


Fig. 2. Raman spectra of the sample prepared by impregnation of zirconia with NH_4VO_3 and H_3PO_4 (P/V atomic ratio 1.1) recorded *in situ* in 3% steam and 14.5% O_2 (remainder N_2) during the isothermal step at 450 °C. Symbols as in Fig. 1.

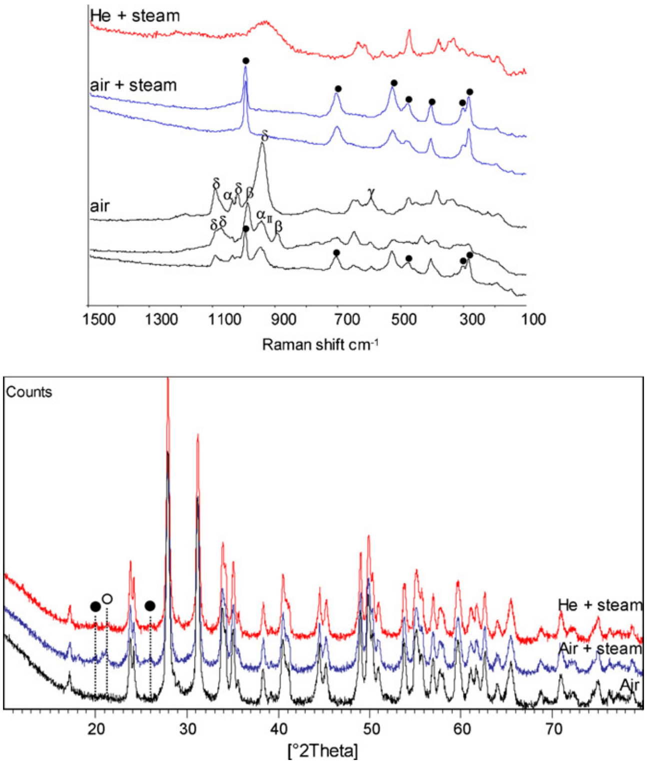


Fig. 3. Raman spectra (top) and X-ray diffraction patterns (bottom) recorded *ex situ* at RT after thermal treatment of the catalyst precursor (P/V 1.1) at 450 °C in different atmospheres: (i) air, (ii) air + 10% steam, and (iii) He + 10% steam. Symbols as in Fig. 1. ○: P_2O_5.

to the stretching vibrations of $P(OH)_2$ [16] and V–O–V in oligomeric VO units [17], respectively. These bands are even more evident when the isothermal step is carried out in a flow of 3% steam in N_2, that is, in the absence of oxygen (spectra not reported). Also in this case, the δ-$VOPO_4$ formed by reaction between ammonium vanadate and phosphoric acid decomposed; however, no bands attributable to bulk V_2O_5 were visible, neither in the spectrum recorded *in situ* at high temperature after 5 h on stream, nor in the spectrum recorded at RT after the treatment. Therefore, under these conditions, δ-$VOPO_4$ evolved into a disordered (amorphous) layer made of polyphosphoric acid and amorphous VO_y.

Thermal treatments were also carried out in tubular muffle, with different types of flowing stream, and with a final temperature of 450 °C. Fig. 3 (top) shows the Raman spectra recorded *ex situ* after thermal treatments for sample P/V 1.1. Also in this case, as shown during the *in situ* experiments, the nature of the compounds formed was a function of the composition of the gas phase used during thermal treatment. When the latter was carried out in a dry air stream, the sample showed bands attributable to various $VOPO_4$ compounds; the sample was not homogeneous, and the beam focusing on several particles gave spectra that showed the presence of different types of vanadium phosphate compounds. When this treatment was done in a 10% steam air flow, the sample obtained was homogeneous, and in all cases bulk V_2O_5 was the prevailing compound. Finally, a treatment carried out in a wet and inert (10% steam in He) stream led to a compound characterized by a Raman spectrum with a dominant broad band centered at around 900 cm^{-1}. The latter may derive from the overlapping of bands due to oligomeric V species and polyphosphoric acid.

Fig. 3 (bottom) shows the corresponding X-ray diffraction patterns. The reflections attributable to monoclinic ZrO_2 were dominant, whereas very weak additional reflections are attributable, with some uncertainty, to V_2O_5 and to P_2O_5; these reflections were more evident in the sample treated in the 10% steam air flow, which agrees with Raman spectra. No clear attribution of any $VOPO_4$ compound could be done from X-ray patterns; however, the very weak reflection at 2θ 29°, observed in the spectrum of the sample treated in air, might be tentatively attributed to α_{II}-$VOPO_4$.

In samples with a P/V ratio of 1.30 and 1.50 (Fig. 4), the spectra recorded *in situ* under flow of 3% steam and 14.5% O_2 in N_2, showed that, in both cases, the δ-$VOPO_4$ formed during heating of the samples was stable and did not decompose into V_2O_5 nor was it transformed into other $VOPO_4$ compounds, within the timeframe of the experiment.

Catalysts were also characterized *ex situ* after reactivity tests. Fig. 5 compares the spectra of fresh samples, after calcination in a 10% steam air flow, and the spectra of the same samples after reaction in *n*-butane oxidation (maximum reaction temperature, 450 °C). Both samples prepared with P/V 1.1 and 1.3 no longer contained δ-$VOPO_4$ after reaction; β-$VOPO_4$ and V_2O_5 were the only compounds present in these samples. Conversely, the sample prepared with P/V 1.5 still showed the presence of the desired δ-$VOPO_4$, as well as smaller quantities of $VOPO_4{\cdot}2H_2O$ and α_I-$VOPO_4$. According to both our previous findings and the role of δ-$VOPO_4$ [6,9–11,18–20], it can be expected that this sample shows the best catalytic performance.

Table 1
Results of catalytic experiments carried out at 400 °C. All samples are made of 10 wt% V/P/O deposited over ZrO_2.

Catalyst	C_4 conv. (%)	Maleic anhydride sel. (%)	CO_x sel. (%)	Lights sel. (%)	Heavies sel. (%)
P/V 1.1	31	5	82	2	11
P/V 1.3	27	10	65	2	23
P/V 1.5	7	18	72	4	6

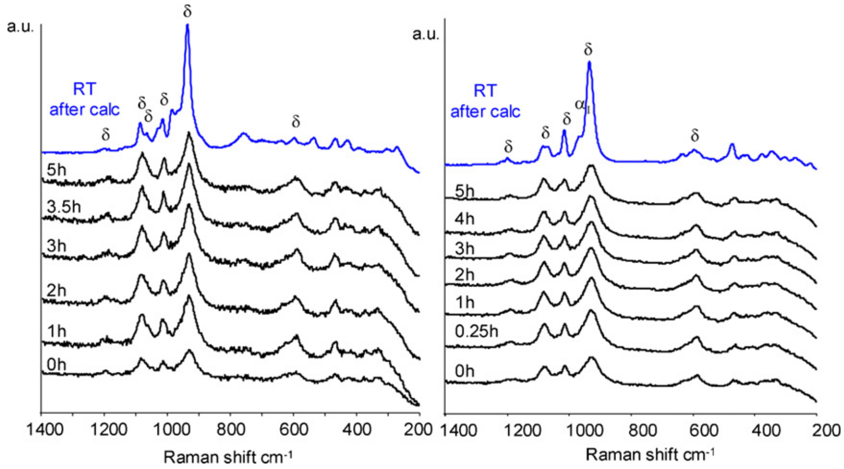


Fig. 4. Raman spectra of the samples prepared by impregnation of zirconia with NH_4VO_3 and H_3PO_4 (figure on the left: P/V = 1.3; figure on the right: P/V = 1.5) recorded *in situ* in a 3% steam air flow during the isothermal step at 450 °C. Symbols as in Fig. 1.

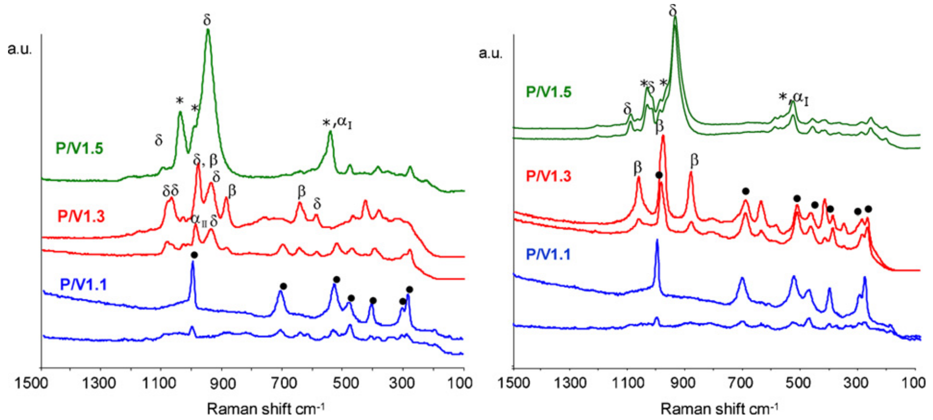


Fig. 5. Raman spectra recorded *ex situ* at RT after thermal treatment of the catalyst precursors at 450 °C in a 10% steam air flow (figure on the left), and after reactivity tests (figure on the right).

3.2. Reactivity tests

Table 1 reports the results of the reactivity tests carried out with samples having P/V atomic ratio of 1.1, 1.3, and 1.5. All the catalysts were firstly calcined in a flow of air with 10% steam (total flow 35 ml/min, $\tau = 0.9$ s) for 5 h at 450 °C, and then treated at 400 °C under reaction conditions for 100 h. This amount of time is necessary for any type of structural or morphological transformation to occur in V/P/O-based catalysts, and is also important for developing an “equilibrated” catalyst with a stable catalytic performance [7]. Catalyst P/V 1.1 was the most active, but it also showed the lowest selectivity to maleic anhydride. It is worth noting that this lower selectivity was not simply a consequence of the higher conversion achieved; in fact, as will be discussed later, also when the comparison is made at similar conversion levels, the selectivity of samples with a P/V ratio of 1.3 and 1.5 was still higher than that of P/V 1.1.

CO_x was not the only by-product of the reaction. In fact, other by-products formed include formaldehyde, acetic acid, acrylic acid, and crotonaldehyde (all of them grouped into “Lights”); however, only small quantities of these light by-products were formed (selectivity less than 4%). Heavier by-products (“Heavies”) also formed, most of which were aromatic compounds; phthalic acid, phthalic anhydride, benzoic acid, and methyltetrahydrobenzoic acid were produced in the greatest amounts.

With regards to P/V 1.5, the catalyst that gave the best selectivity to maleic anhydride, the details of the selectivity to the various classes of products as a function of the reaction temperature are shown in Fig. 6. The selectivity to Heavies increased when the reaction temperature was increased, with a concomitant decrease in the selectivity to carbon oxides. On the contrary, the selectivity to maleic anhydride was not much affected, and the same was observed for the selectivity to Lights. This behavior, together with the nature of heavy by-products, suggests that the formation of these compounds most likely occurs thanks to the condensation

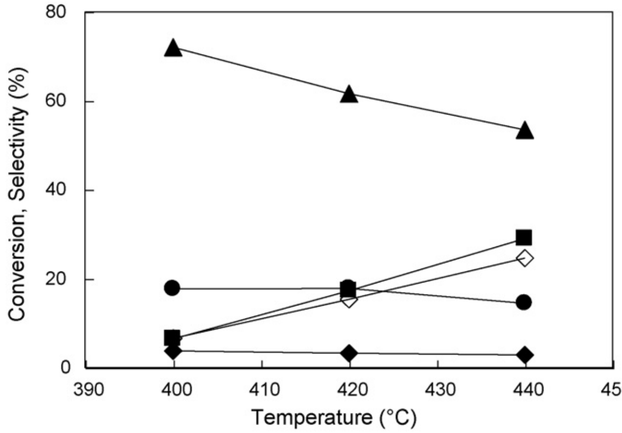
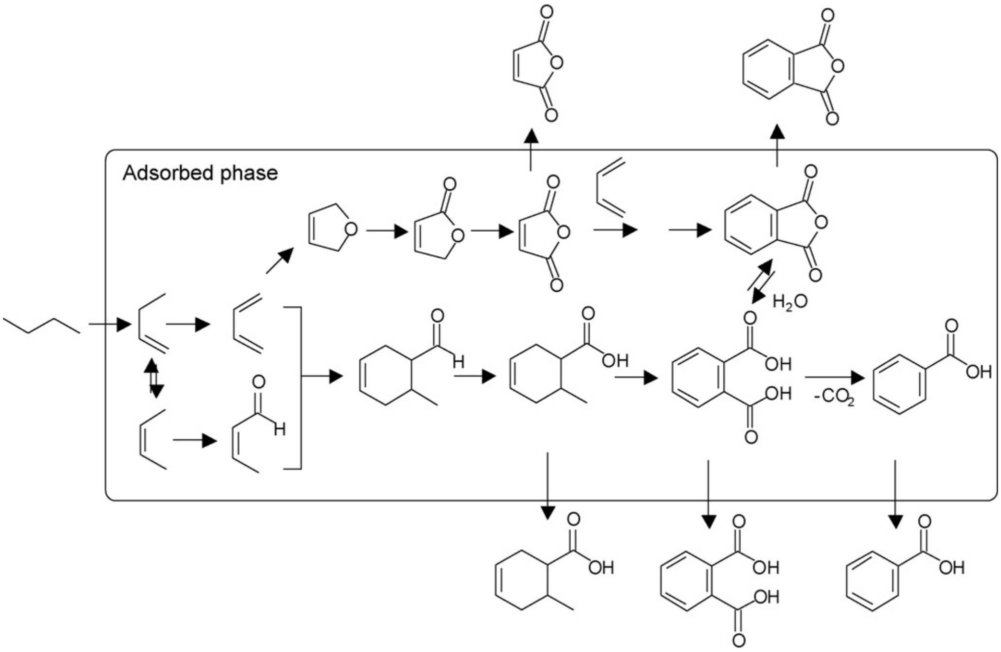


Fig. 6. Results of catalytic experiments as a function of temperature with P/V 1.5 catalyst. Symbols: *n*-butane conversion (◇), selectivity to maleic anhydride (δ), to COx (▲), to Lights (◆) and to Heavies (■).



Scheme 1. Surface mechanism suggested for the transformation of *n*-butane to maleic anhydride, CO_x and heavy compounds with zirconia-supported V/P/O catalysts.

Table 2
Amount of acid sites in P/V 1.1 and P/V 1.5 samples, as measured from pyridine adsorption measurements (IR spectra recorded at increasing temperature).

Catalyst	T (°C)	C_B (μmol/g)	C_L (μmol/g)
P/V 1.1	25	28	23
	200	19	13
	450	0	2
P/V 1.5	25	14	17
	200	6	9
	450	0	1

of unsaturated intermediates. One hypothesis is that the condensation reaction may occur in the presence of acid sites, and that the latter are generated *in situ* by hydrolysis of either $VOPO_4$ or polyphosphoric acid. In fact, the selectivity to Heavies, achieved at similar levels of *n*-butane conversion, increased in the following order:

P/V 1.1 (selectivity 11% at 31% *n*-butane conversion) < P/V 1.3 (selectivity 23% at 27% *n*-butane conversion) < P/V 1.5 (selectivity 29% at 25% *n*-butane conversion).

It is worth noting that under the conditions used, heavy compounds desorbed into the gas phase, and were not retained on the catalyst surface. In fact, no relevant short-term deactivation phenomena were observed.

In order to confirm the role of surface acid sites, we carried out further characterization and reactivity experiments with P/V 1.1 and P/V 1.5 samples.

3.3. *The role of surface acidity on reactivity behavior*

Table 2 compares the amount of acid sites, as inferred from the IR spectra recorded after adsorption of pyridine and desorption at increasing temperature. Sample P/V 1.5 had a greater number of acid sites than P/V 1.1, especially of the Brϕnsted-type; the acidity level, however, was not very different in the two cases, thus indicating that the nature of the sites was similar for the two samples. According to the literature concerning the acidity of VPP and of V/P/O compounds in general, Brϕnsted sites are attributable to P–OH groups [21]; Lewis sites can be tentatively attributed either to coordinatively unsaturated V^{5+} sites, or to Zr^{4+} sites (in fact, the acidity characterization of the zirconia support highlighted the presence of Lewis-type sites, and no Brϕnsted acid sites whatsoever). It is worth noting that the surface acidity of VPP is strong enough to catalyze reactions such as aromatic ring alkylation or glycerol dehydration [22,23].

P–OH sites are generated by the hydrolysis of either V/P/O compounds or polyphosphoric acids. Therefore, the concentration of sites responsible for heavy compounds formation should be a function of steam partial pressure. Water is a co-product of the reaction, and its partial pressure increases in parallel with the conversion of *n*-butane, which should enhance the hydrolysis phenomena, thus contrasting the dehydration reaction that is thermodynamically favored when the reaction temperature is increased. In order to confirm this hypothesis, we carried out reactivity tests by co-feeding an additional amount of steam (10% in the inlet stream), with the P/V 1.1 and 1.5 catalysts. The results of this experiment

Table 3
Reactivity of P/V 1.1 and P/V 1.5, both in the absence and in the presence of co-fed steam.

Catalyst	Steam in feed (%)	T (°C)	C_4 conv. (%)	Maleic anhydride sel. (%)	CO_x sel. (%)	Heavies sel. (%)	Maleic acid sel. (%)	Lights sel. (%)
P/V 1.1	0	400	31	5	82	11	tr	2
	10	400	28	3	72	18	5	1
P/V 1.5	0	440	25	15	53	29	tr	3
	10	420	26	9	32	43	14	2
	10	440	40	9	35	35	19	2

are shown in Table 3. With both samples, the addition of steam led to an increase in the selectivity to Heavies, with a concomitant decrease in the selectivity to CO_x. In the case of P/V 1.5 however, this variation was greater than with P/V 1.1. Moreover, with both catalysts, a relevant increase in the selectivity to maleic acid (which was formed only in trace amounts under conventional reaction conditions), and a decrease in the selectivity to maleic anhydride were observed.

4. Discussion

From the literature, it is clear that many authors have tried to prepare catalysts made of supported VPP [24–37]. This was achieved either by preparing samples in the presence of precursors for the formation of both the support and the active V/P/O phase, or by depositing the components, precursors for the active phase formation, onto the support, e.g., titania, alumina, silica or Al phosphate [24–33]. With model VO-systems, for catalysts containing approximate monolayer coverage of surface vanadia, the number of converted *n*-butane molecules per vanadium atom was a strong function of the specific oxide support [34]. In most cases, however, the intrinsic characteristics of the VPP were worsened due to the chemical interaction that develops between the active phase and the support. One exception was the catalyst prepared by Ledoux et al. [35,36], who studied the use of heat-conducting supports (β-SiC, Si_3N_4 and BN) for VPP. This catalyst significantly increased the maleic anhydride yield with respect to the unsupported one, because of the better control of the catalyst surface temperature. Moreover, the support apparently did not affect the chemical properties or the reactivity of the VPP. Outstanding performances were also obtained by Au et al. [37], who used V/P/O catalysts supported on ZrO_2 and H_3PO_4-treated ZrO_2 by means of precipitation–deposition in an organic medium.

With our samples, the approach used was different to that reported in the literature. We did not try to develop the VPP precursor, $VOHPO_4 \cdot 0.5H_2O$ (a V^{4+} compound), by carrying out the synthesis in the presence of the support; conversely, we decided to build-up the desired δ-$VOPO_4$, starting from a V^{5+} salt and phosphoric acid. Under reaction conditions, one can expect equilibrium to be reached between δ-$VOPO_4$ and VPP, because structural similarities between the two compounds facilitate structural interconversion during the redox process.

The role of $VOPO_4$ compounds in the redox behavior of V/P/O-based catalysts for *n*-butane oxidation to maleic anhydride is known since long time [14,15,38–42], but the exact structure of some of the various $VOPO_4$ polymorphs still is under debate [43–45]. For example, the structure of α_I-$VOPO_4$ has not yet been resolved; this compound, observed in some of our samples, reversibly transforms into $VOPO_4 \cdot 2H_2O$ by hydration [14,38]. Concerning the δ-$VOPO_4$, this compound was first reported by Bordes [38], who proposed that this compound is isostructural with $VOAsO_4$, featuring pairs of edge-sharing octahedral, like VPP. This led to the hypothesis that VPP and δ-$VOPO_4$ may easily interconvert. The structure of δ-$VOPO_4$ has been recently resolved [45]. The structure contains infinite chains of trans corner-sharing VO_6 octahedra which run parallel to [1 0 0] and [0 1 0] directions. Each VO_6 shares single corners with four different phosphate groups, and each phosphate connects four different chains of VO_6. The main peculiarity of the δ structure is that it contains an unusually long V–O contact (3.1 Å); moreover, it is more strained than other $VOPO_4$ polymorphs.

In our previous investigations [10,11], we found that the P/V ratio is a critical parameter that affects the type of $VOPO_4$ that is finally obtained; this has also been confirmed with the samples reported in the present study. In this case, however, a large excess of P is needed not only to develop the desired δ-$VOPO_4$ during thermal treatment, but also to hinder its consecutive transformation into other, undesired $VOPO_4$ compounds or its complete hydrolysis into V_2O_5 and polyphosphoric acid [46].

The sample prepared with a P/V ratio of 1.5 gave the highest selectivity to maleic anhydride, and the lowest selectivity to carbon oxides. This confirms that the best performance is achieved with the catalyst whose active component is made mainly of δ-$VOPO_4$. On the other hand, the excess of P loaded is responsible for the generation of Brϕnsted-type acid sites, which catalyzed the condensation or addition-type reaction between intermediates to form heavy compounds. For a *n*-butane conversion of 25–30%, the selectivity to these latter products is the highest with the P/V 1.5 catalyst, and is further enhanced with both P/V 1.1 and P/V 1.5 samples when the partial pressure of steam in the gas phase is very high.

Let us discuss the reaction mechanism for the formation of these heavy by-products. Reaction intermediates are butenes, butadiene, crotonaldehyde and dihydrofuran [47,48] (Scheme 1). The nature of the heavy compounds formed suggests that a Diels-Alder-type addition between butadiene and crotonaldehyde (both products being obtained from butenes) may lead to the formation of 2-methyltetrahydrobenzaldehyde and, subsequently, of the corresponding acid derivative (one of the heavy products identified). The latter may then be oxidized to phthalic acid and phthalic anhydride, whereas benzoic acid likely forms by decarboxylation of phthalic acid. On the other hand, the olefinic intermediates may either be oxidized to maleic anhydride, or to carbon oxides. The relative rate of the three parallel reactions (which have common reaction intermediates) is a function of the reaction temperature, the partial pressure of steam (an increase of which increases the rate of the reaction leading to the formation of the heavy compounds), and catalyst composition.

Diels-Alder reactions are catalyzed by both Brϕnsted and Lewis acid systems [49]. In general, these reactions are conducted at room temperature or slightly elevated temperatures, because of the instability of reactants and products, and because in many cases reactions are exoenthalpic but reversible, hence the formation of products may be unfavored at high temperature. In our case, however, the presence of an oxidizing environment may shift the equilibrium towards the formation of products, because the primary addition product – the ring-substituted cyclohexene – is oxidized to yield the corresponding aromatic compounds. Therefore, P-OH Brønsted-type acid sites, present in the catalyst having a large excess of P, may accelerate the reaction between unsaturated intermediates to generate heavy compounds. Acid systems also catalyze the reaction of butadiene with maleic anhydride [50], a reaction that also may contribute to phthalic anhydride and phthalic acid formation [51,52].

All in all, the performance of the catalysts prepared is worse than that of the unsupported VPP catalyst, and of some silica-supported V/P/O catalysts described in the literature [53,54]. There are various reasons for this:

(a) The large number of acid sites, arising from the high loading of P, which in turn is necessary to develop and maintain the δ-$VOPO_4$ compound. The formation of heavy compounds is favored by acidity.

(b) In unsupported VPP, the latter and the δ-$VOPO_4$ are in redox equilibrium, and they catalyze the transformation of *n*-butane to maleic anhydride with high selectivity. The rate-determining step is V^{4+} oxidation, and hence VPP is the prevailing compound in the equilibrated catalyst [12]. A limited amount of δ-$VOPO_4$ develops at the surface of VPP by V^{4+} oxidation, thus providing a moderate concentration of oxidizing V^{5+} sites. Finally, this results in mild oxidation, rather than total oxidation. On the other hand, when the catalyst is made of δ-$VOPO_4$, as in the case of our supported P/V 1.5 catalyst, the development of a reduced V^{4+}-containing active phase may be a more difficult process. Therefore, the supported catalyst is too oxidizing, and the formation of carbon oxides is kinetically favored over the formation of maleic anhydride. In other words, the presence of VPP as the main component of the active phase is essential in providing a controlled and optimized number of oxidizing sites.

5. Conclusions

Supported V/P/O catalysts for *n*-butane oxidation to maleic anhydride were prepared by means of the impregnation of zirconia with ammonium vanadate and phosphoric acid, and by thermal treatment under various environments and temperatures. The nature of the active surface was found to be greatly affected by both the composition of the gas phase used for the thermal treatment, and the P/V ratio used for catalyst preparation. δ-$VOPO_4$ was initially formed by high-temperature reactions between the vanadium salt and phosphoric acid; however, in the sample with P/V = 1.1, δ-$VOPO_4$ transformed into either V_2O_5, in a steam-enriched air stream, or β-$VOPO_4$, in a dry air stream. The δ-$VOPO_4$ was more stable in the sample prepared with a large excess of P, i.e., with P/V = 1.3 and 1.5. The latter catalyst showed the best catalytic performance in *n*-butane oxidation. However, the selectivity to maleic anhydride was no greater than 20%, mainly because of the production of heavy compounds. The latter formed by the acid-catalyzed addition between unsaturated intermediates, and oxidative dehydrogenation of the addition product to form aromatic oxygenated compounds. The number of surface Brϕnsted sites was highest in the catalyst prepared with P/V 1.5, which also provided the greatest selectivity to the undesired heavy by-products.

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