

Influence of the oxidation state of vanadium on the reactivity of V/P/O, catalyst for the oxidation of *n*-pentane to maleic and phthalic anhydrides

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Abstract

In this paper the role of V⁵⁺ and V³⁺ ions in V/P/O, catalyst for the oxidation of *n*-pentane to maleic and phthalic anhydrides, has been investigated. These species have transient lifetime, since the stable, fully equilibrated catalyst only contains vanadyl pyrophosphate, (VO)₂P₂O₇, and V⁴⁺ ions. Therefore, first the formation of V⁵⁺ and V³⁺ species has been induced in catalysts, either by means of a suitable oxidative treatment on a equilibrated V/P/O catalyst, to generate controlled amounts of V⁵⁺, or by adopting a preparation procedure which leads to the formation of discrete amounts of V³⁺ in fresh catalysts. Thereafter, the evolution of catalytic performance was followed along with time-on-stream. A relationship was found between the distribution of products, and the oxidation state of V in catalysts. Higher concentrations of V⁵⁺ led to the preferred formation of maleic anhydride, while samples having average V valence state close to 4.00+ and well-crystallized vanadyl pyrophosphate were the most selective to phthalic anhydride. The latter samples were also characterized by the higher Lewis-type acid strength. The reduced catalyst, containing a large amount of V³⁺ ions, was instead non selective towards either of phthalic and maleic anhydrides; the progressive catalyst oxidation in the reaction environment led to the increase in the yield to both products.

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1. Introduction

Vanadyl pyrophosphate (VPP) is the main component of the industrial V/P/O catalyst for the oxidation of *n*-butane to maleic anhydride (MA), and also catalyzes the oxidation of *n*-pentane to maleic and phthalic anhydrides (PA) [1–4]. Even though vanadium is present as V⁴⁺ in stoichiometric VPP, the role of V species other than V⁴⁺ on the catalytic behavior of V/P/O has been the object of debate for many years [5–13]. This derives from the evidence that the fresh catalyst, i.e., the V/P/O obtained by thermal treatment of the crystalline precursor VOHPO₄·0.5H₂O, contains crystalline and amorphous vanadium phosphates other than (VO)₂P₂O₇ [14,15]. These addi-

tional phases may contain V⁵⁺ or even V³⁺, and the relative amount of each compound is a function of (i) the procedure employed for the preparation of precursor, and (ii) the thermal treatment adopted for the transformation of the precursor. Furthermore, the VPP itself may host V ions other than V⁴⁺ as defects, without undergoing substantial structural changes; specifically, the possible development of either V³⁺ or V⁵⁺, even in considerable amounts, has been demonstrated [16–18]. Outer surface layers of V⁵⁺ phosphates may develop in the reaction environment, and play active roles in the catalytic cycle.

Concerning the role of V⁵⁺ on catalytic performance in *n*-butane oxidation, sometimes contradictory results have been reported in literature, but the main reason for this is related to substantial differences in chemical–physical features of the samples (which are affected by the preparation procedure), and by different ageing times. Volta and his co-workers [5–7] demonstrated that V⁵⁺ micro-domains may develop at the surface of

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VPP (without the formation of any VOPO₄ phase), the presence of which leads to an improvement in selectivity to MA, while the conversion of *n*-butane remains substantially unaffected. An optimal V⁵⁺/V⁴⁺ surface ratio, equal to 0.25, gives the best selectivity to MA. The development of any bulk VOPO₄ phase, instead, has a detrimental effect on catalytic performance. Other authors confirmed the important role of V⁵⁺, which develops on the surface of the VPP during reaction [8–13].

One further consideration is that the distribution of V species in equilibrated VPP may be a function of the reaction conditions. This might explain contradictions in literature concerning the amount of V ions other than V⁴⁺ in catalysts, since reaction conditions are changed from those typical of fixed-bed applications (with *n*-butane concentrations in air lower than 1.7%), to those of fluidized-bed processes (3–4% *n*-butane), and to very high *n*-butane-to-oxygen ratios in the CFBR reactor [1–4,19,20]. Therefore, on one hand the distribution of V species can be considerably affected by reaction conditions, but on the other hand the nature and surface density of the different species may affect the distribution of the products. Also, the possible addition of dopants can represent one way to modify the nature of surface V species, and tune the catalytic performance in function of the reaction conditions [7].

Much less studied has been the role of V species in *n*-pentane oxidation to MA and PA, a reaction which is also catalyzed by V/P/O. Many papers have been published in the period 1985–2000, aimed at the determination of (i) the reaction mechanism for the formation of PA, and (ii) the V/P/O properties which may affect the overall selectivity to MA + PA, and the ratio between the two anhydrides; fewer papers have been published in recent years [21,22]. Most works have pointed out the importance of having well-crystallized VPP in order to address the transformation of the hydrocarbon to PA rather than to MA [23–26]. Only in one paper, it was proposed that a higher oxidation state of vanadium in V/P/O chiefly gives MA, while a lower valence state is necessary for the formation of PA [27].

Aim of the present work was to study the effect of the presence of V⁵⁺ and V³⁺ species on catalytic performance of V/P/O, in the oxidation of *n*-pentane to MA and PA. The formation of these V species was induced either by suitable oxidizing treatments of a fully equilibrated catalyst, or by proper thermal treatments of the VPP precursor. These V species undergo quick transformation under reaction conditions, but their transient catalytic performance may furnish indications on their role in the formation of products. Moreover, in the case of *n*-pentane oxidation, relationships can be searched for between catalyst features and performance, especially in terms of distribution of products. In

fact, the reaction mechanism for MA and PA formation includes steps in which both surface acidity and redox properties play an important role [24].

2. Experimental

Different V/P/O samples were prepared, in order to investigate a wide range of catalyst characteristics. Sample 1 was prepared according to the following procedure: the catalyst precursor, VOHPO₄·0.5H₂O, was precipitated starting from a suspension of 8.2 g V₂O₅ (Aldrich, purity 99.6+%) and 10.1 g H₃PO₄ (Aldrich 98+%) in 75 ml isobutyl alcohol (Aldrich, 99%+); the suspension was heated under reflux conditions for 6 h. The precipitate obtained was filtered, washed with a large excess of isobutyl alcohol and dried at 125 °C overnight. After a spray-drying conglomeration of particles into fluidizable material [28], the compound was thermally treated to develop the VPP structure, using the hydrothermal-like procedure described in detail elsewhere [29]. The thermal treatment was aimed at the development of a well-crystallized VPP, which took shorter time to reach the equilibrated state under reaction conditions, with respect to conventional thermal treatments. Then, the catalyst was run in a fluidized-bed pilot reactor for three months, under the following conditions: temperature 400 °C, feed 4% *n*-butane in air, pressure 3 atm. After this period, the catalyst was downloaded by cooling the reactor under reaction feed. This sample is designated as sample 1eqfresh. Sample 1eqfresh was then oxidized in air, under different conditions (see Table 1), in order to develop discrete amounts of V⁵⁺. Samples obtained were designated as 1(oxa)fresh, 1(oxb)fresh and 1(oxc)fresh; they were then used for catalytic tests in a lab reactor. Corresponding samples downloaded after catalytic tests are denoted with the suffix spent.

Sample 2 was prepared with a procedure which consists of the use of mixtures of isobutyl alcohol and glycols [30,31] as reducing agents for V₂O₅; specifically, a mixture of isobutyl alcohol (80 vol.%) and 1,3-propanediol (20 vol.%) was used. During the synthesis of the precursor, the water generated by reduction of vanadium oxide was refluxed into the slurry. The precursor obtained contained large amounts of organic compounds retained in the inter-layer spacing of its lamellar structure [30,31]. The removal of organic compounds from the precursor, either intentionally added [14] or retained during the preparation [31], by thermal treatment may generate either oxidized [14] or reduced [31] V/P/O phases, depending on the procedure adopted and the amount of organics originally present in samples. The thermal treatment of sample 2 was carried out as follows: first,

Table 1
Main chemical–physical features of catalysts before catalytic tests

Sample	Oxidizing treatment in air, time (h), <i>T</i> (°C)	Surface area (m ² /g)	(V ⁵⁺ /V _{tot}) × 100	(V ³⁺ /V _{tot}) × 100
1eqfresh	None	21	0	0.5–1
1(oxa)fresh	4, 450	17	3.5	0
1(oxb)fresh	4, 500	n.d.	5.2	0
1(oxc)fresh	4, 550	14	47	0
2fresh	None	13	0	18

pre-treatment in air (flow 130 ml/min) from room temperature to 300 °C (temperature gradient, 1°/min), and secondly treatment in N₂ (flow 20 ml/min) from 300 °C to 550 °C (temperature gradient 1°/min), with a final isothermal step in N₂ flow of 6 h. In this case, a strongly reduced catalyst develops [31]. The sample obtained after the thermal treatment was designated as *2fresh*; corresponding sample downloaded after catalytic tests in lab reactor is designated as *2spent*.

Catalysts were characterized by means of X-ray diffraction (Phillips diffractometer PW3710, with Cu K α as radiation source), UV–vis–diffuse reflectance (DR) spectroscopy (Perkin-Elmer Lambda 19), and chemical analysis. The amount of residual C content in samples was determined by combustion in pure oxygen at 1300 °C, with detection of CO₂ formed by infrared analysis (instrument ELTRA 900CS).

Measurements of surface acidity was carried out by recording transmission FT-IR spectra of samples pressed into self-supported disks, after adsorption of pyridine at room temperature, followed by stepwise desorption under dynamic vacuum at increasing temperature (Perkin-Elmer mod 1700 instrument).

The procedure for chemical analysis consisted of the dissolution of 1 g of sample in hot concentrated H₂SO₄. Then, after cooling of the solution, V⁵⁺ was directly determined by titration with a Fe²⁺ solution, while the amount of V³⁺ + V⁴⁺ was determined by titration with MnO₄⁻. The latter solution, which exclusively contains V⁵⁺ after titration, was then titrated with Fe²⁺, to determine the overall amount of V. Special precautions to be used and limitations of the technique are reported in Ref. [17].

Catalytic tests of *n*-pentane oxidation were carried out in a laboratory glass flow-reactor, operating at atmospheric pressure, loading 3 g of catalyst diluted with inert material. Feed composition was: 1 mol% *n*-pentane in air; residence time was 2 g s/ml. The temperature of reaction was varied from 320 to 420 °C. The products were collected and analyzed by means of gas chromatography. An HP-1 column (FID) was used for the separation of C₅ hydrocarbons, MA and PA. A Carbosieve SII column (TCD) was used for the separation of oxygen, carbon monoxide and carbon dioxide.

Due to variations in the characteristics of samples under reaction conditions, catalytic tests were arranged in a way to obtain reliable relationships between the average oxidation state of V in samples and catalytic performance. The problem was particularly relevant when tests were carried out on oxidized catalysts (samples 1(*ox*)*fresh*); in fact, in the latter samples the average oxidation state of V lowered considerably in a few hours. Therefore, for each catalyst and for each reaction temperature, the reactivity data were collected immediately after loading the *fresh* catalyst in the reactor. In this case, therefore, it can be assumed that the results obtained were representative of chemical–physical features of the *fresh* catalysts. Then, at each temperature level, the reaction was carried out for a few hours more, and reactivity results were obtained again. After this, the catalyst was cooled in nitrogen flow, downloaded and analyzed. Therefore, the second set of data can be collected as a representative of the chemical–physical features of *spent* catalysts. As a consequence of the procedure adopted, several *spent*

Table 2

Main chemical–physical features of catalysts downloaded after reaction in *n*-pentane oxidation

Sample	Surface area (m ² /g)	(V ⁵⁺ /V _{tot}) × 100	(V ³⁺ /V _{tot}) × 100
1eq <i>spent</i>	21	0	0.5–1
1(<i>oxa</i>) <i>spent</i>	21	0	1–2 ^a
1(<i>oxb</i>) <i>spent</i>	n.d.	2.0–2.5 ^a	0
1(<i>oxc</i>) <i>spent</i>	16	28	0
2 <i>spent</i>	24	0	1

^a See Section 2 for explanation of intervals.

samples (one for each temperature level) were obtained starting from the same *fresh* catalyst; the former usually had similar XRD patterns and similar UV–vis–DR spectra, while small differences were found by chemical analysis. This is the reason for the ranges of values for V oxidation state, which are indicated in Table 2 for *spent* samples.

3. Results

3.1. The characterization and reactivity of samples obtained by oxidation of a fully equilibrated V/P/O catalyst

Table 1 summarizes the main chemical features, surface area and distribution of V species as determined by chemical analysis, for samples 1*fresh*. Sample 1eq*fresh* was a fully equilibrated catalyst, while samples 1(*oxn*)*fresh* were obtained by controlled oxidizing treatments of sample 1eq*fresh*. The procedure adopted for this treatment is also given in the table; more severe conditions led to the generation of an higher amount of V⁵⁺. Sample 1eq*fresh* did not contain V⁵⁺ at all; the catalyst had been operating with 4 mol% *n*-butane in air, which are the conditions adopted in industrial fluidized-bed processes.

Figs. 1 and 2 report the corresponding X-ray diffraction patterns and UV–vis–DR spectra, for samples 1*fresh*. XRD patterns of all samples, but 1(*oxc*)*fresh*, correspond to that of well-crystallized VPP; in the case of sample 1(*oxc*)*fresh*, reflections marked with the asterisk are attributable to VOPO₄ (37-0809), and more specifically to the δ form of this compound [32]. In

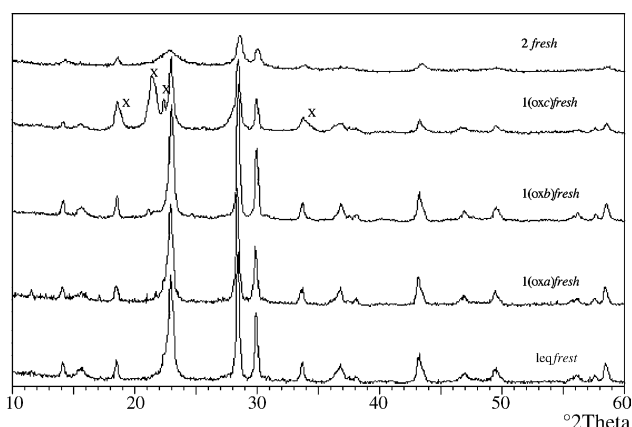
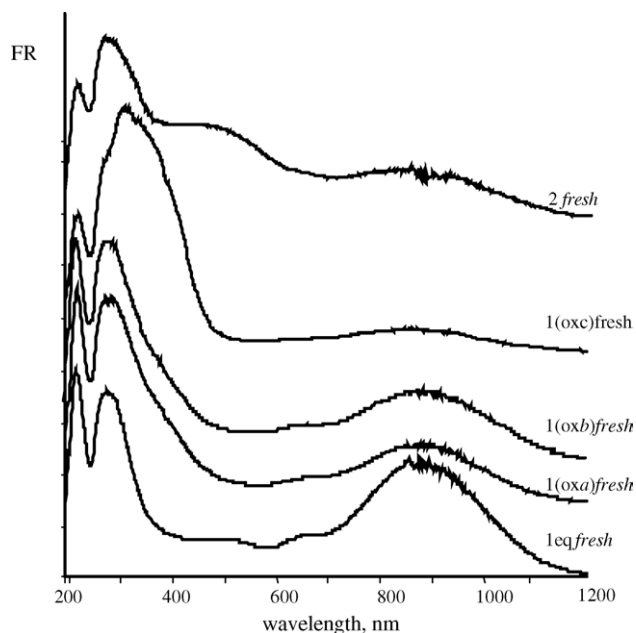


Fig. 1. X-ray diffraction patterns of *fresh* samples x = reflections relative to δ -VOPO₄.

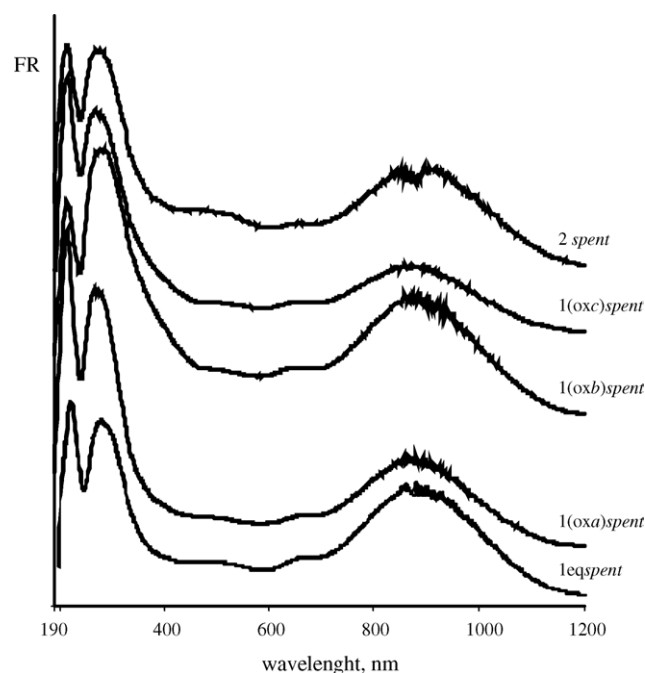
Fig. 2. UV-vis-DR spectra of *fresh* samples.

UV-vis-DR spectra (Fig. 2), the band at 400 nm is relative to the CT between O^{2-} and V^{5+} ; its intensity is proportional to the amount of V^{5+} . On the other hand, the band at 900 nm, relative to a d-d transition for V^{4+} in VO^{2+} , correspondingly decreases.

It has been reported that the introduction of V^{5+} ions as defects in VPP occurs after treatment at more severe conditions than those here employed, and leads to a collapse of surface area and to a broadening and a lowering of intensity for all reflections in the pattern [18]. In other cases, modification in the XRD pattern involve mainly the (200) reflection, thus suggesting a preferential structural disorder along the [1 0 0] axis induced by the development of V^{5+} species in the bulk [5]. In our case, the treatment of the VPP probably led to the generation of surface V^{5+} in samples 1(oxa)*fresh* and 1(oxb)*fresh*, and to the growth of $VOPO_4$ in sample 1(oxc)*fresh*.

Table 2 reports the chemical analysis of the *spent* samples, after reaction in *n*-pentane oxidation. It is shown that catalysts after reaction were more reduced than the corresponding samples before reaction. Sample 1(oxa)*spent* was fully reduced, and did contain a low amount of V^{3+} ; samples 1(oxb)*spent* and 1(oxc)*spent*, instead, yet retained some fraction of V^{5+} . This is also evident from Fig. 3, which reports the corresponding UV-vis-DR spectra. The intensity of the band at 400 nm was lower than in corresponding *fresh* samples (Fig. 2); in the case of catalysts 1eq*spent* and 1(oxa)*spent* this band was absent. Therefore, the V^{5+} species is not stable in the reaction environment, and is progressively reduced to V^{4+} . In addition, a weak band at 500 nm, attributed to the V^{3+} species [17], was present in samples 1eq*spent* and 1(oxa)*spent*.

Fig. 4 plots the distribution of surface acid sites as determined by adsorption of pyridine for samples 1eq*spent*, 1(oxa)*spent* and 1(oxc)*spent*. Specifically, the amount of residual pyridine adsorbed on Brønsted and Lewis sites, after desorption at each temperature, is plotted as a function of the evacuation tempera-

Fig. 3. UV-vis-DR spectra of *spent* samples.

ture. All samples exhibited a predominance of Lewis-type acid sites, and the residual amount of adsorbed pyridine after evacuation at 400°C was very low; this indicates that the Lewis-type acid sites had a medium-strength acidity. A scale of relative acidity can be drawn, which is slightly different if based on the overall number of acid sites (that is, based on the amount of pyridine adsorbed after evacuation at room temperature), or if based on the distribution of acid strength. In the former case, the scale of acidity was: 1(oxa)*spent* > 1eq*spent* > 1(oxc)*spent*. In the latter case, the catalyst possessing the largest fraction of sites with the higher strength was sample 1eq*spent*. The latter sample did not possess Brønsted acidity at all either, while sam-

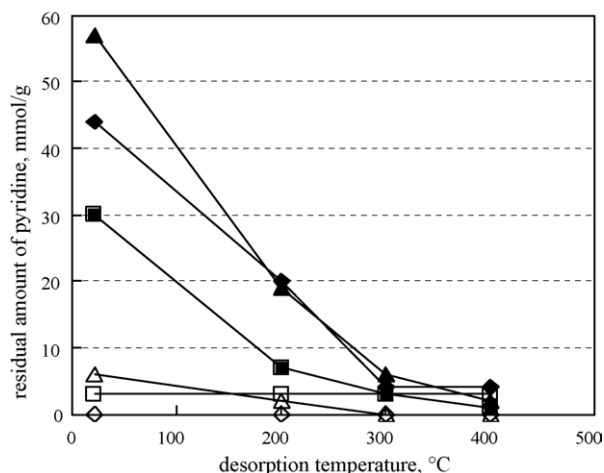


Fig. 4. Amount of residual adsorbed pyridine as a function of desorption temperature (after adsorption at room temperature) for samples 1eq*spent* and 1(oxn)*spent*. Open symbols: pyridine adsorbed on Brønsted sites; Full symbols: pyridine adsorbed on Lewis sites. Catalysts: 1eq*spent* (◆), 1(oxa)*spent* (▲), 1(oxc)*spent* (■).

ple 1(*oxc*)*spent* had Brønsted sites which still retained pyridine after evacuation at high temperature, and thus can be classified as strong ones. In the case of sample 1(*oxa*)*spent*, no pyridine remained adsorbed on Brønsted sites after evacuation at 300 °C.

The stronger Lewis-type acidity in the equilibrated catalyst is not surprising, since there are many literature evidence of the existence of these sites in well-crystallized VPP [33]. Also, the presence of a discrete amount of V³⁺ ions has been assumed to contribute to an enhancement of catalyst Lewis-type acidity, due to the development of anionic vacancies [16,34]. The Brønsted acidity in the oxidized catalyst (sample 1(*oxc*)*spent*) can be associated with the presence of P–OH groups arising from the transformation of pyrophosphate groups into orthophosphate.

Catalytic tests were carried out following the protocol described in Section 2. Specifically, within the first 5–10 h reaction time, the catalytic performance was not stable, due to variations in samples characteristics. Therefore, two different sets of data were obtained, the first after less than 1 h (representative of *fresh* samples), and the second one after 3–4 h (representative of *spent* samples). Only in the case of sample 1eq, no difference was found between the characteristics of samples 1eq*fresh* and 1eq*spent* (Tables 1 and 2); for this catalyst, the catalytic performance did not vary at all during catalytic tests either. This means that variations of catalyst characteristics were negligible due to the permanence of the catalyst under hydrocarbon-lean conditions (more oxidant than those employed for equilibration in pilot plant).

Fig. 5 reports the catalytic performance of sample 1eq*fresh*; the conversion of *n*-pentane, and the selectivity to the main products, MA, PA and carbon oxides, are reported as functions of the reaction temperature. The selectivity to MA increased with increasing reaction temperature, and correspondingly the selectivity to PA decreased. The overall selectivity to PA and MA slightly decreased, due to the preferred formation of carbon oxides. This behavior was observed for all samples. The opposite trend for MA and PA was due to the fact that the two parallel reactions, starting from the unsaturated C₅ intermediate and leading to the formation of the two products, occur through different mechanisms [35].

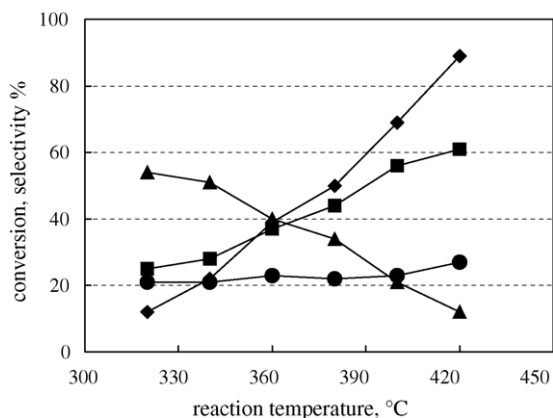


Fig. 5. Effect of temperature on *n*-pentane conversion (◆), selectivity to MA (■) to PA (▲), and to CO_x (●). Catalyst 1eq*fresh*.

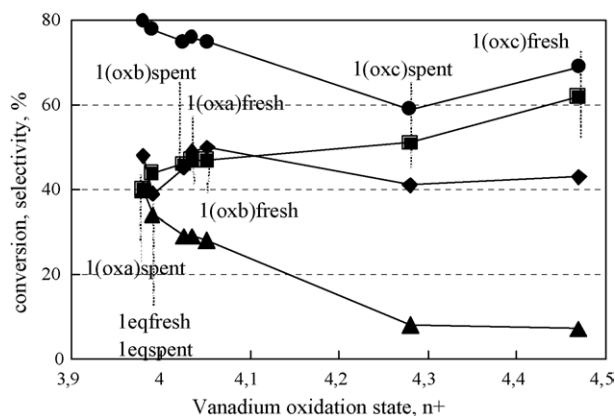


Fig. 6. Conversion of *n*-pentane at 360 °C (◆), and selectivity to MA (■), to PA (▲) and to MA + PA (●) at 43–50% *n*-pentane conversion as functions of the average oxidation state of V in samples 1.

Fig. 6 summarizes the results obtained for both *fresh* and *spent* samples; the conversion reached at the temperature of 360 °C, and the selectivity to MA and to PA at approximately 43–50% *n*-pentane conversion, are plotted as functions of the average oxidation state of V. The more oxidized was the catalyst, the more preferred was the formation of MA with respect to that of PA, with a MA/PA selectivity ratio equal to 7 at 50% *n*-pentane conversion for sample 1(*oxc*)*fresh*. The opposite was true for most reduced samples, with a MA/PA selectivity ratio around 1. The decrease of selectivity to PA, with increasing values of V oxidation state, was much more relevant than the corresponding increase in MA; therefore, the overall selectivity to the products of partial oxidation (MA + PA) decreased with increasing extents of V oxidation, from 80% for sample 1(*oxa*)*spent* to 59% for sample 1(*oxc*)*spent*. The exception was sample 1(*oxc*)*fresh* (the most oxidized one), which gave an overall selectivity to MA + PA equal to 68%.

3.2. The characterization and reactivity of a reduced, non-equilibrated V/P/O catalyst

One alternative procedure for developing samples having controlled amounts of V species other than V⁴⁺ in V/P/O, starts from the precursor VOHPO₄·0.5H₂O, and makes use of specific thermal treatments. The precursor contains discrete amounts of organic compounds retained in its lamellar structure, which remain entrapped during the crystallization. Its amount is a function of the nature of the organic reductant used during the preparation [30,31]. Specifically, if linear alcohols, glycols, or other reductants are used which may easily diffuse into the inter-layer space of the lamellar precursor, the amount of organic compounds which are retained can be as high as a few wt.% C. In contrast, when branched-chain molecules are used, e.g., isobutyl alcohol, the amount of retained compounds is lower than 1 wt.% C. The removal of these organic compounds during the thermal treatment occurs in the same range of temperature as for the transformation of the precursor into VPP. Therefore, when the thermal treatment is done in air, the combustion of organic compounds may cause a local over-heating and the development of

VOPO₄ compounds in place of VPP. The same occurs when the organic compound (e.g., stearic acid) is intentionally added to the precursor to favour the tableting procedure [14]. For this reason, it is necessary to carry out a pre-treatment at temperature not higher than 300 °C and under controlled atmosphere, in order to remove most of the organic deposits without any structural transformation of the precursor, and finally realize the development of the VPP under inert atmosphere (N₂) [30,31]. On the other hand, if the initial removal of the organics under oxidizing atmosphere is incomplete (this is the case, for instance, when its amount in the precursor is higher than 4–5 wt.% C), during the high-temperature treatment in N₂, the organic compounds are transformed to CO₂ by picking up the bulk ionic oxygen of the VPP. In consequence of this, the final catalyst may be considerably reduced, and contain amorphous and/or crystalline V³⁺ phosphates [30,31].

Reduced V/P/O compounds are also obtained when the precursors are prepared using either (i) isobutyl alcohol as the reducing agent, under water reflux during the synthesis of the precursor, and a thermal treatment with only N₂ at $T > 400$ °C, without oxidative pre-treatment [23,36], or (ii) isobutyl alcohol with water withdrawal, and a thermal treatment consisting of a pre-calcination in air at 300 °C, followed by treatment in N₂ at $T > 450$ °C [17], or (iii) isobutyl alcohol/benzyl alcohol mixtures, under water reflux, followed by a thermal treatment analogous to that employed for sample *2fresh* [15]. Therefore, thermal treatments are to be carried out carefully [29], in order to obtain a V/P/O which is as crystalline as possible, contains a low amount of compounds other than VPP, and finally does not require too long reaction times for equilibration [14,15,36].

On the other hand, the preparation of precursors containing controlled amounts of organic compounds, and a proper thermal treatment of the precursor itself, can be used to endow the V/P/O catalyst with specific properties. In our case, the procedure described in Section 2 was adopted to obtain an extensive reduction degree for sample *2fresh*; the corresponding precursor contained 2.8 wt.% C [31]. Sample *2fresh* was rather amorphous, but reflections attributable to VPP could be distinguished (Fig. 1). The presence of V³⁺ in the calcined sample was also confirmed by chemical analysis (Table 1), and by UV–vis-DR spectra (Fig. 2); in the latter case, the very intense band at 500 nm due to the presence of the V³⁺ species appeared [17].

While in the case of samples *1(ox)fresh*, obtained by oxidation of an equilibrated VPP, the modification of catalyst characteristics and performance occurred within a few hours under reaction conditions, in the case of sample *2fresh* corresponding changes were much slower, and full equilibration took more than 200 h time-on-stream. This was likely due to the fact that the structural modifications involved the entire bulk of the catalyst, whereas modifications induced by oxidation of the equilibrated VPP (samples *1(ox)fresh*) were limited to the external part of grains; therefore, a much shorter reaction time was necessary to restore the original situation.

The slower changes of sample *2fresh* made it possible to follow the variation of catalytic performance, which is reported in Fig. 7 as a function of reaction time, at 400 °C. During this equilibration time, the main variation was the oxidation of V³⁺

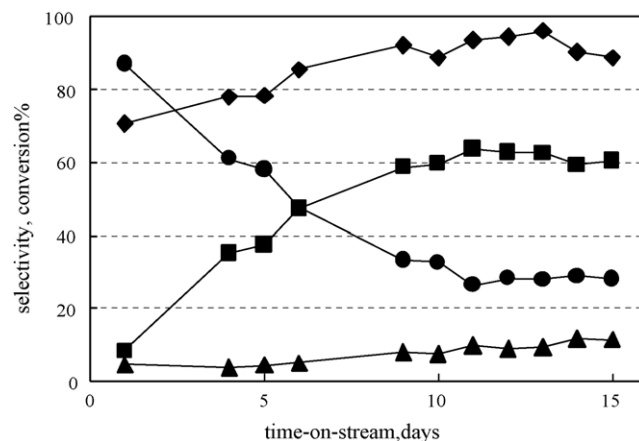


Fig. 7. Conversion of *n*-pentane (◆), selectivity to MA (■), to PA (▲) and to COx (●) as functions of time-on-stream, at 400 °C. Catalyst *2fresh*.

to V⁴⁺ (Table 2), which corresponded to the decrease of intensity of the band at 500 nm in the UV–vis-DR spectrum (Fig. 3), and was also accompanied by an increase in the sample crystallinity. The fresh catalyst was active, but poorly selective; the prevailing products were carbon oxides. The progressive oxidation of V³⁺ led to an increase in catalyst activity, to a remarkable increase in the selectivity to MA, and to a smaller one for the selectivity to PA.

4. Discussion

In order to better understand the role of each V species, it is useful to summarize the different hypothesis reported in literature, concerning the mechanism of *n*-pentane oxidation. The main controversial point is whether MA and PA are formed through parallel reactions starting from a common intermediate, or, on the contrary, MA is consecutively converted to PA. In regard to the former hypothesis, it has been proposed that *n*-pentane is first oxydehydrogenated to pentene and pentadiene; the latter can be either oxidized to MA (with the loss of one C atom), or be transformed to cyclopentadiene, which then dimerizes to a cyclic template and is finally oxidized to PA [37–39]. An alternative route to PA is through an acid-assisted dimerization and dehydrocyclization of intermediate pentadiene to yield a cyclic, 6C-membered ring, aliphatic C₁₀ hydrocarbon, precursor of an alkylaromatic compound, which is finally oxidized to PA and 2 COx [24,35,40]. This latter mechanism is illustrated in Fig. 8. Other authors suggest that *n*-pentane is either transformed to isopentane (precursor of citraconic anhydride), or to butene and butadiene; the latter is oxidized to MA, and finally a Diels–Alder reaction between MA and adsorbed butadiene leads to the formation of PA [21]. In this case, therefore, MA consecutively forms PA.

Whatever the mechanism for PA formation is, the combination of the redox and acid properties of the catalyst determines the relative contribution for the formation of MA and PA. This is also inferred from an analysis of the catalysts characteristics which are claimed in literature to be relevant to the catalytic performance in *n*-pentane oxidation:

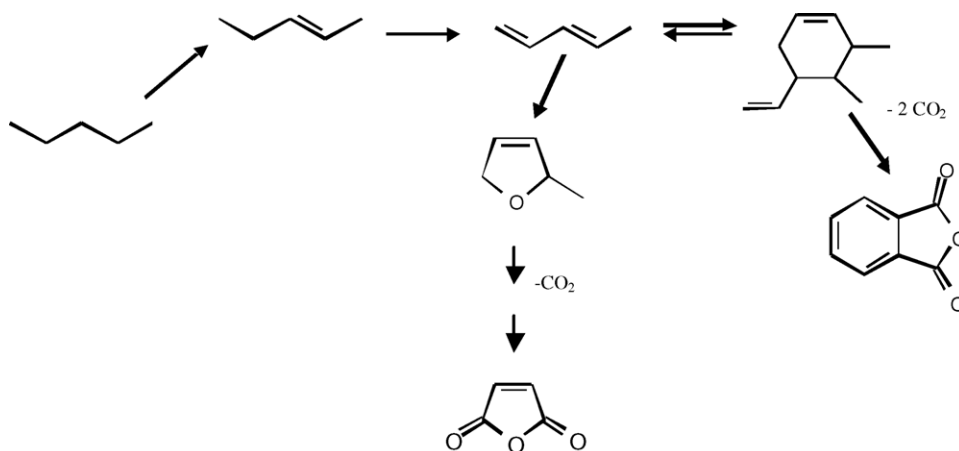


Fig. 8. Mechanism for *n*-pentane oxidation to MA and PA.

- (a) The higher the crystallinity of the VPP, the more selective to PA is the catalyst [14,23–26,35,36,41,42]. Poorly crystalline VPP, such as forms after the thermal treatment of the precursor (especially when it is carried out under oxidizing conditions), is selective to MA, but non-selective to PA. On the other hand, a fully equilibrated catalyst characterized by the presence of a well-crystallized VPP, yields PA with a good selectivity. The presence of dopants which alter the crystallinity may finally affect the MA/PA selectivity ratio [43].
- (b) The surface acidity also affects the selectivity [35,44]; an increase in Lewis acidity improves the selectivity to PA, while that to MA is positively affected by Brønsted acidity [21]. Also, an increase in acidity improves the formation of citraconic anhydride.

Data reported in the present work demonstrate that the amount of V^{5+} , generated by controlled oxidation of a well-crystallized VPP, considerably affects the selectivity to MA and PA. In general, oxidized V/P/O catalysts are more selective to MA and less to PA (Fig. 6), while the selectivities to the two products become comparable with the equilibrated V/P/O catalyst, in which the amount of V^{5+} is very low. Therefore, in strongly oxidized catalysts, the olefinic intermediate is preferentially oxidized to MA, rather than being subjected to condensation reactions with a second unsaturated molecule to yield the precursor of PA. The preferred formation of MA over oxidized VPP may be due either to a direct role of V^{5+} and of *O*-insertion sites, which make the pathway leading to MA quicker than the parallel one to PA, or to the fact that the arrangement of sites at the surface of well-crystallized VPP is a necessary condition for the development of a specific interaction with the unsaturated intermediate and for the transformation to PA [23–26,35,36,41,42]. The development of surface layers of $VOPO_4$ over VPP suppress the interaction between the latter and reactants or intermediates, with a consequent lower rate for PA formation.

For what concerns the role of acidity, the comparison of data reported in Figs. 4 and 6 indicates that the strongest Lewis acidity in less oxidized catalysts (samples 1eqspent and 1(oxa)spent) favours the reaction pathway which leads to the formation of PA.

In fact, these samples are those which give the higher selectivity to PA at 43–50% *n*-pentane conversion. This supports the view that the specific properties of well-crystallized VPP in the formation of PA are related to its remarkable Lewis-type acidity.

The performance of the reduced sample (2fresh) was peculiar; it was quite unselective to MA and PA, but the selectivity to these compounds progressively recovered along with V^{3+} oxidation. The selectivity to PA remained lower than 15%; however, it is worth mentioning that at 400 °C, and at high *n*-pentane conversion, the selectivity to PA was not higher than 20% even for those samples which were more selective to this compound (see, for instance, Fig. 5 for sample 1eqfresh).

5. Conclusions

The transient reactivity of V/P/O catalysts, containing discrete amounts of V^{5+} or V^{3+} ions (generated either by controlled oxidation of an equilibrated VPP, or by specific preparation procedures), has been examined, in order to establish the role of these species in the mechanism for the formation of MA and PA in *n*-pentane oxidation. A relationship was found between the amount of V^{5+} species and the MA/PA selectivity ratio measured at approximately 50% *n*-pentane conversion; specifically, more oxidized catalysts were more selective to MA and less to PA, while with less oxidized samples the selectivity to the two products was comparable. The former catalysts were also those having the lower Lewis-type acid strength, which is supposed to play an important role in the mechanism for the formation of PA. It was confirmed that the crystallinity of VPP is also an important factor which positively affects the rate of PA formation. Strongly reduced V/P/O catalysts were poorly selective to MA and to PA, but the progressive increase in V oxidation state and the development of crystalline VPP led to a progressive increase in the selectivity to the two compounds.

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