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VPO catalyst for *n*-butane oxidation to maleic anhydride: A goal achieved, or a still open challenge?

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This review describes recent findings in the oxidation of *n*-butane to maleic anhydride. The process is commercial since the 80's, but yet the yield is far from being optimised. Therefore, it represents an emblematic example of how several scientific disciplines, from solid-state science to reactor technology, can contribute to the improvement of the process performance.

KEY WORDS: Vanadyl pyrophosphate; *n*-butane; selective oxidation; maleic anhydride

1. The oxidation of *n*-butane catalysed by VPO: How to improve process performance?

The activation of light alkanes by high-temperature contact with a redox catalyst represents one way to transform these hydrocarbons to valuable chemicals (a few reviews and books dealing with this topic, published after 1998, are refs [1–18]). The most successful example is the oxidation of *n*-butane to maleic anhydride (MA), catalysed by a V/P/O-based catalyst (VPO), which starting from the 80's has been replacing in part the commercial synthesis from benzene. This reaction, and the unique chemical–physical properties of the vanadyl pyrophosphate $(VO)_2P_2O_7$ (VPP), the active and selective phase for this reaction, are amongst the most studied topics in catalysis during the latest decades, initially with the aim of understanding which catalyst peculiarities make this complex transformation possible, and later on with the aim of improving the process performance.

MA finds its major use in the production of unsaturated polyesters and of butanediol. The yearly world consumption exceeds 1.3×10^6 metric tons [19]. Approximately 70% is produced by *n*-butane oxidation, the remaining still being obtained from benzene. There are several reactor technologies available, including fixed-bed (Scientific Design, Huntsman, BASF, Pantochim), fluidised-bed (Lonza, BP, Mitsubishi), and transported-bed (DuPont). Best process performances reported in patent literature range from 53 to 65% molar yield to MA [20–25], with a conversion of the hydrocarbon not higher than 85–86%. An excellent result of more than 70% yield is reported [26], which however refers to a recycle process. In lab reactors best yields reported are lower than 50%.

The best performance for a fixed-bed reactor does not exceed 65% per-pass yield, while that in a fluidised-bed is typically somewhat lower; in fact, back-mixing phenomena are responsible for the consecutive combustion of MA. Moreover, with fluidised-bed operation *n*-butane-richer conditions can be used (up to 5 molar % in feed); under the latter conditions, a worsening of selectivity is expected, which however is compensated by a considerable improvement in MA productivity. In the fluidised-bed process developed by Lonza and Lummus (shown in figure 1), the loss of selectivity is also compensated by the higher amount of high-pressure steam produced, due to the more efficient removal of the reaction heat and to the more CO_x produced.

The maximum yield to MA is limited by the following factors:

(a) The presence of parallel reactions of *n*-butane combustion and of oxidative degradation to acetic and acrylic acids. These are characterised by higher activation energies with respect to the main reaction.
(b) The presence of consecutive reactions of combustion, which lower the selectivity to MA when the alkane conversion is increased. However, while up to 60–70% *n*-butane conversion the extent of the consecutive combustion, although present, is not considerable, the decrease in selectivity becomes dramatic over 70–80% conversion. This has been attributed to the development of local catalyst overheating, due to the high reaction exothermicity, and to the poor heat-transfer properties of the catalytic material. This problem is obviously more important in fixed-bed than in other reactor configurations characterised by better heat-transfer properties.

Options proposed to overcome the mentioned limitations are the following:

(a) To modify the redox and acid–base properties of the active phase by addition of specific dopants.

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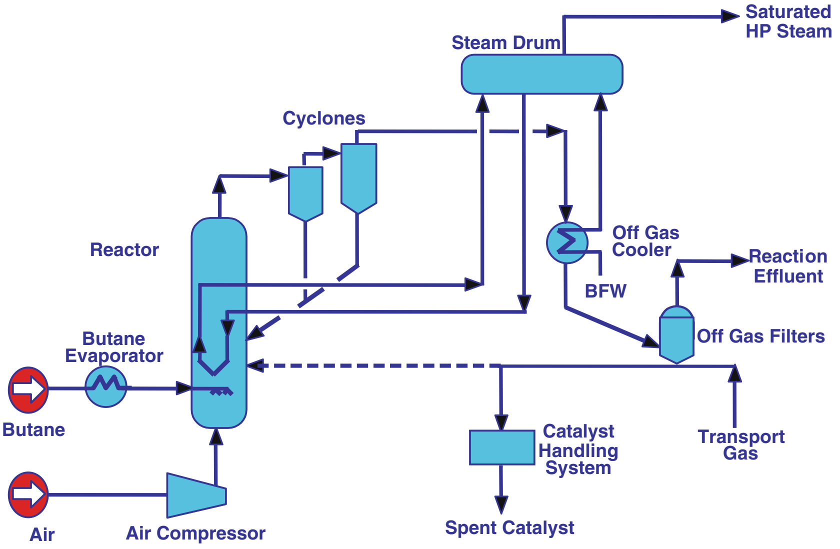

Figure 1. Simplified flow-sheet of the reaction section of the Lonza ALMA process for maleic anhydride production.

Alternatively, to develop new procedures for the preparation of the catalyst that allow a modification of the chemical–physical or morphological features of the precursor (e.g., increase of the surface area), and finally of VPO.

(b) To use highly heat-conductive supports for VPO, in order to better distribute the reaction heat and develop a more homogeneous particle temperature.

(c) To operate at low *n*-butane conversion, with recycle of the unconverted hydrocarbon. This implies two different options: (i) Feed pure oxygen, or oxygen-enriched air, to the process (hydrocarbon-rich conditions). Very high conversion of oxygen is reached, so to keep its concentration below the MOC. (ii) Use hydrocarbon-lean conditions, more favourable for selectivity, and feed air or oxygen-enriched air. The conversion of *n*-butane, the limiting reactant, is kept low and unconverted *n*-butane is recycled after separation from those inert components that are not maintained in the recycle loop. In this way, it is possible to obtain better selectivity to MA, because of the lower per-pass conversion, but the process productivity is low.

(d) To limit the oxygen fed to the reactor, or to control its concentration inside the reactor by staging it along the bed, so to keep high local hydrocarbon-to-oxygen ratios. The extrapolation of this concept is the transported-bed technology developed by DuPont, and operated in a semi-commercial unit in Spain. In this technology, the catalyst is shuttled between a net oxidising and a net reducing environment, inside a circulating fluidised-bed reactor [27,28]. However, this unit has been recently shut down.

These different options are now examined in detail.

2. The modification of VPP properties by the addition of dopants

The numbers of scientific papers devoted to the study of promoters for VPO has been growing in recent years, despite it seemed that in the 80's all the possible dopants for this catalyst had been already investigated [29–32]. In fact, a more profound knowledge of the chemical physical properties of the VPP has made possible a better comprehension of the role of dopants, the promotional effect of which had been already preliminarily evaluated in the past. This is the case of Co and Fe [33–40], and of Bi [41]. A new type of promoter for VPO, mentioned in an early ICI patent [42] and later on claimed by Matsuura *et al.* [43], is Nb [44–46]. This element promotes the catalyst activity through generation of surface defects, to which Lewis acid sites are likely associated, that participate in the activation of the alkane. Results on several dopants for VPO, reported in recently published scientific papers, are summarised in table 1.

It seems that the use of promoters represents the most promising approach for the improvement of the catalytic performance of VPO. Milestones in this direction have been already defined, due to the fact that the most important features affecting the catalytic performance of VPP are known. It is nevertheless obvious that a deep comprehension of the mechanisms through which promoters affect these features is still far from being fully understood.

3. Other options for modifications of VPP chemical–physical properties

Other options for the modification of the VPP properties have been investigated, and include:

Table 1
Summary of recent achievements on the effect of promoters on VPO performance

Dopant, optimal amount	Promotional effect[a]	Reasons for promotion	Ref.
Co, Co/V 0.77%	C 15 → 25% and S 0 → 11%, under hydrocarbon-rich conditions	Control of the optimal V^{5+}/V^{4+} surface ratio; stabilisation of an amorphous Co/V/P/O compound	[33–36]
Co, Co/V 13%	C 55 → 79% and S 43 → 35%, at 653 K	Optimal surface Lewis acidity	[37–40]
Ce + Fe	C 44 → 60% and S 63 → 66% in the absence of O_2	Improvement of redox properties	[47]
Fe, Fe/V 0.08	Increase of catalytic activity	Fe replaces V^{4+} in $(VO)_2P_2O_7$. The re-oxidation rate is increased	[48,49]
Ga, Ga/V 0.10	C 22 → 73% and S 55 → 51%	Increase of surface area + increase of intrinsic activity (electronic effect)	[50]
Nb, 0.25 wt%	C 20 → 17% and S 35 → 53%	Increase of surface acidity promotes desorption of MA	[44]
Nb, Nb/V 0.01	C 58 → 75% and S 70 → 70%	Nb concentrates at the surface, where defects are generated. Nb acts a *n*-type dopant; development of a more oxidised surface	[45]

[a] C = conversion; Y = yield; S = selectivity for the undoped → doped catalysts, at fixed reaction conditions.

(a) Modification of the synthetic procedure for $VOHPO_4 \cdot 0.5H_4O$, the precursor of VPP, e.g., use of oxygenated compounds other than isobutanol. When the "organic" preparation is employed, with isobutanol as the reductant for vanadia, various additional organic compounds can be used in order to affect the morphology of the precursor [51–55]. Intercalation of the compounds in the lamellar structure of the precursor occurs with (i) benzyl alcohol [51], (ii) linear and branched-chain aliphatic alcohols [52], and (iii) primary *n*-alkylamines [53]; these compounds alter the interlayer spacing. The same effect can be obtained starting from $VOPO_4 \cdot 2H_2O$ [54], or in the preparation of vanadyl alkylphosphonates, where the interlayer spacing increases with increasing carbon chain length [55]. The synthesis done in the presence of aliphatic alcohols leads to the development of vanadyl alkylphosphonates of lamellar morphology, where the d(001) value correlates with the molecular length of the starting alcohol, and in which the construction of the basal plane is similar to that of $VOHPO_4 \cdot 0.5H_4O$ [56]. When instead aldehydes or ketones are used, the product of the reaction between V_2O_5 and H_3PO_4 is $VO(H_2PO_4)_2$ [57]. The calcination of these hybrid precursors sometimes leads to the VPP, but none of the catalysts obtained performs as well as the VPP synthesised with the conventional procedure. One exception is the preparation using polyethyleneglycol as additive, which gives rise to the formation of a highly active and selective catalyst [58,59]. In this case, the main effect on VPP properties is an increase of surface area: 41 m^2/g as compared to 16 m^2/g for the conventional preparation. Maximum yield to MA is 65%, that represents an improvement with respect to the preparation with isobutanol/benzyl alcohol.

The preparation of the precursor in the presence of glycols (1,2-etandiol, 1,3-propandiol, 1,4-butandiol) affects the morphology of the precursor [60,61]. Reported in table 2 are the main characteristics of some samples: the type and amount of glycol used (the remainder being isobutanol), and the amount of organic compounds retained in the precursor. The latter was similar for the two shorter-chain alcohols 1,2-ethandiol and 1,3-propandiol, while it was lower (and the same) for the two butandiol isomers. Therefore it seems that the size of the molecule plays a role in determining the maximum amount of glycol which can be trapped in the interlayer spacing of the precursor, in agreement with literature data obtained using other types of alcohols [54,72]. The

Table 2
Main characteristics of the precursors prepared with isobutanol/glycols mixtures

Sample	Glycol, vol%[A]	Amount of organics retained			FWHM [220]/FWHM [001]
		a	*b*	*c*	
1	–	0.6	0.9	0.012	0.70
2	1,2-ethandiol, 20	2.3	5.9	0.095	0.46
3	1,3-propandiol, 20	2.8	5.9	0.078	0.32
4	1,3-butandiol, 20	1.6	3.0	0.033	0.65
5	1,4-butandiol, 20	1.6	3.0	0.033	0.57

a: Amount of organic compounds retained, wt% C; *b*: Amount of glycol retained, wt% (calculated assuming that the glycol is the only organic compound retained); *c*: Amount of glycol retained, mol/g_{cat} %.
[A] Remainder is isobutanol.

importance of the reactant size is also demonstrated by the much lower amount of alcohol that is retained when only isobutanol (a branched-chain compound) is used (sample 1 in table 2).

A relationship exists between the organics content in the precursor and the "aspect ratio" of the crystal. Increasing amounts of retained organic compounds disturb the stacking of crystallographic planes along the *c* direction, and only [*hk0*] reflections remain sharp for the higher C contents. Correspondingly, the aspect ratio changes considerably, indicating the development of crystals having different morphology, as also confirmed by SEM micrographs. The thermal treatment included (i) a pre-calcination step in air up to 300 °C [60,61], aimed at the desorption and oxidation of as much as possible of the organic compounds without over-reduction or amorphisation of the vanadyl orthophosphate, and (ii) a high-temperature treatment in N_2, to complete the transformation of the precursor into the VPP. An alternative heat treatment under hydrothermal-like conditions was claimed [62], which made possible a better control of the characteristics of the final catalyst. The thermal treatment is a crucial step to determine the morphology of the VPP [63]. It was also found that for defined ranges of organics amount retained in the precursor, it is possible to infer a controlled defectivity to the final VPP [60], with a limited number of V^{3+} species. These catalysts were more active than those obtained from the precursor prepared in the absence of glycols [61].

In an alternative preparation, the precursor is done in aqueous medium, using HCl as the reductant for vanadia. However, this procedure can be carried out even at high temperature and in the absence of HCl; a compound develops having high surface area, comparable to that of the precursor prepared by the "organic" procedure [64]. The VPP obtained by transformation of this precursor exhibits a catalytic performance similar to that of the material obtained by the conventional preparation.

(b) Tribomechanical (ball-milling) activation of the precursor or of the VPP. The idea was first reported by Horowitz *et al.* [52], and later applied by other authors [65,66]. Ball-milling of the precursor is carried out with the aim of increasing the surface area by reducing particle size; this results in higher catalyst activity [67]. However, also lattice imperfections are introduced, as a consequence of the high energy used for milling; these defects are transferred to the VPP during transformation of the precursor, and finally affect the catalytic performance [68]. This leads to an improvement of the activity and selectivity.

(c) Intercalation of layered $VOPO_4 \cdot 2H_2O$ with various compounds (e.g., alcohols, amines), followed by exfoliation in polar solvents into delaminated sheets; finally, impregnation of silica with the solution containing the delaminated layers [69–71]. The same procedure can be adopted to reduce the $VOPO_4 \cdot 2H_2O$ into $VOHPO_4 \cdot 0.5H_2O$ [72,73], to obtain a high-surface-area precursor and finally a VPP that is more active and selective than that one prepared by conventional procedures (60% conversion, 78% selectivity at 390 °C) [71]. Dispersion of VPP inside or over high-surface-area silica was also tried by other researchers, but in general this procedure did not lead to active catalysts [74–76].

(d) Preparation of an amorphous, microspheroidal VPO catalyst using supercritical CO_2 as an antisolvent [77,78]. The amorphous compound was claimed to be intrinsically (i.e., per unit surface area) more active than crystalline VPP, and did not require extensive activation periods to reach stable performance. However, a maximum yield to MA of only 7% was reported.

(e) Preparation of mesostructured VPO phases and of VPO/surfactant composites [79–84]. Guliants *et al.* described the preparation of microporous mesostructured VPO with surfactants as structure-directing agents and optimised the thermal treatment and template removal, obtaining systems characterised by high surface area. However, these systems were not stable under reaction conditions, and transformed into various VPO dense phases. The selectivity to MA was fairly good at low *n*-butane conversion, but fell for increasing hydrocarbon conversions.

4. The use of highly-heat-conducting supports

One of the most significant improvement in *n*-butane oxidation has been reported by Ledoux *et al.*, who studied the use of heat-conducting supports (β-SiC, thermal conductivity 140–270 W/m K, Si_3N_4, 6 W/m K, and BN, 31 W/m K) for the VPP [85,86]. The peculiarity of the materials employed is the relatively high surface area (e.g., for β-SiC, >20 m^2/g, prepared via the "shape memory synthesis"), which makes them useful as supports for exothermal oxidation reactions [87]. These catalysts gave a significant gain in MA yield when used in a fixed-bed reactor, because of the better control of the catalyst surface temperature. Moreover, the chemical inertness of the support did not modify the reactivity properties of the precursor and of VPP, which instead is what happens with conventional supports [88]. In the case of the β-SiC-supported VPO (30 wt% of active phase), the selectivity to MA at high *n*-butane conversion was higher than that obtained with the unsupported catalyst. An even more relevant result was reported under *n*-butane-rich conditions (e.g., O_2/*n*-butane feed ratio 3.2, with 11 mol% *n*-butane), with 72% alkane conversion and 54% MA yield at 485 °C. This represents the best result ever reported for *n*-butane oxidation under hydrocarbon-rich conditions. Moreover, the thermal stability of the supported VPO was greatly enhanced with respect to that of the bulk catalyst. The former material could withstand thermal treatments up to 620 °C without any worsening of the catalytic performance at 380–480 °C. The heat-conductive support also protected the catalyst against accidental temperature excursions.

5. New catalysts for *n*-butane oxidation

New types of catalytic systems are being investigated. In the past, it was demonstrated that Keggin-type P/Mo/V polyoxometalates are fairly active and selective in the oxidation of *n*-butane [89]. Recently, it has been reported that the pyridine salt of Nb-exchanged molydo(vanado)phosphoric acid is the precursor of a catalyst, mostly consisting of amorphous molybdenum oxide, which is active and selective in the oxidation of propane to acrylic acid and of *n*-butane to maleic anhydride [90–92]. The authors found that key-properties to achieve good catalytic performance are (i) the development of reduced Mo^{5+} and Nb^{4+} species, that are stable species when hydrocarbon-rich reaction conditions are used, and (ii) the contemporaneous presence of P, Nb and pyridine in the polyoxometalate (pyridine acts as the reductant for Mo^{6+} during the thermal treatment). Catalysts are active under both *n*-butane-rich and *n*-butane-lean conditions. The best performance reported is 90% selectivity at 15% conversion at 380 °C, under *n*-butane-rich conditions (with total oxygen conversion), and 62% conversion with 46% selectivity at 340 °C, under hydrocarbon-lean conditions (2% *n*-butane in feed).

6. Reactivity under *n*-butane-rich conditions, and the role of the different V species

The oxidation state of V in VPP under working conditions and the role of the different V species in the reaction mechanism, have been the object of scientific debates for several years. The importance of having a defined amount of V^{5+} in order to obtain better selectivity has been pointed out by Volta and co-workers, the optimal V^{5+}/V^{4+} ratio being equal to 0.25 [93–97]. Evidences for the role of V^{5+} have also been reported by other authors [98–101]. Isolated V^{5+} sites in strong interaction with the VPP are those responsible for the activation of the alkane and for O-insertion, while the formation of bulk $VOPO_4$ is detrimental for selectivity.

More controversial is the role of V^{3+}; the generation of V^{3+}/P/O compounds is negative for selectivity, but the development of a discrete number of these species in the VPP lattice, and the associated anionic vacancies, were proposed to play a positive role on catalytic activity [102–105]. V^{3+} defects are generated during the thermal treatment of the precursor, and the number of defects is a function of (i) the amount of organics retained in the precursor, and (ii) the nature of the heat treatment carried out for the transformation of the precursor into the active catalyst [18].

The oxidation state of V in VPP under working conditions is a function of reaction conditions and, more specifically, of the gas-phase composition. First papers dealing with the reactivity of VPO under hydrocarbon-rich conditions were published by Centi *et al.* [106,107]. It was established that one important factor in order to catalyse the multi-step transformation of the alkane to MA is the surface availability of O-insertion sites. Specifically, it was found that at high hydrocarbon-to-oxygen ratio, the scarce availability of these sites makes the transformation of reaction intermediates (i.e., butenes and butadiene) slower, and causes the desorption of these compounds into the gas phase; this leads to a lower selectivity to MA.

Operation at high hydrocarbon partial pressure (i.e., under reducing conditions, with O_2 as the limiting reactant), can offer considerable advantages with respect to the hydrocarbon-lean conditions: (i) an increase of the productivity for the same reactor volume, or, alternatively, a reduced vessel size (less catalyst inventory); (ii) a more concentrated product stream, with lower costs for MA recovery; and (iii) better heat transfer properties of the feed stream, depending on the type of ballast maintained in the recycle loop (typically, CO_2). The problem is to avoid the formation of flammable mixtures. In regard to this, the fluidised-bed process is more flexible, since it can operate inside the flammable area, provided the hydrocarbon is directly injected in the fluidised solid volume. Industrial operation is carried out with 4–5 mol% *n*-butane in feed, almost three times the concentration normally used in fixed-bed apparatus (the lower flammable limit of *n*-butane in air is 1.8 mol%). More concentrated *n*-butane streams are used in the case of transported-bed technology. One way to circumvent the problem in fixed-bed is to stage the oxygen, so to stay below the MOC all along the reactor. Pantochim [108] has claimed fixed-bed operation with O_2 instead of air, and with recycle of non-condensable gases to have a suitable amount of ballast inside the reactor.

Mallada *et al.* [109], investigated the effect of reducing (hydrocarbon-rich) and oxidising (hydrocarbon-lean) conditions on the oxidation level of the catalyst. In the former case, V^{3+}/P/O surface phases developed, which were detrimental for the selectivity to MA. At the same time, substantial amounts of C deposits accumulated on the catalyst, in the fraction of bed that operated under low oxygen partial pressure. The same conclusions were reached by Volta *et al.* [110]: the reduction of V^{5+} and the formation of C deposits were responsible for the decrease of the selectivity to MA. One way to overcome these limitations is to add promoters that help to maintain a higher V oxidation degree, probably through the formation of specific compounds, or through a mediation of V re-oxidation in the redox mechanism. Also, the catalyst morphology is an important parameter under hydrocarbon-rich conditions, more than under leaner conditions [111]. The rose-petals-like morphology gave the most active and selective catalyst, thanks to the higher V reducibility and re-oxidisability as compared to VPP having a different morphology.

The kinetics of the reaction under *n*-butane-rich conditions was recently studied by two research groups [112–115]. C deposits build up on the reduced V sites under reducing conditions. Barteau *et al.* found that the lattice oxygen of VPP only takes account of a minor fraction of the reaction [116], and that therefore a major contribution derives from adsorbed oxygen species, as already proposed in the past [117].

A detailed investigation of the reaction products obtained with different gas-phase compositions evidenced the possible formation of heavy by-products when the *n*-butane concentration in feed is higher than 5–6% [118]. It was found that the availability of gas-phase oxygen affects the nature of the by-products obtained. Under conditions of total oxygen conversion, the formation of tetrahydrophthalic and phthalic anhydrides, by Diels–Alder reaction between unsaturated C_4 intermediates and MA, becomes a competitive reaction (figure 2).

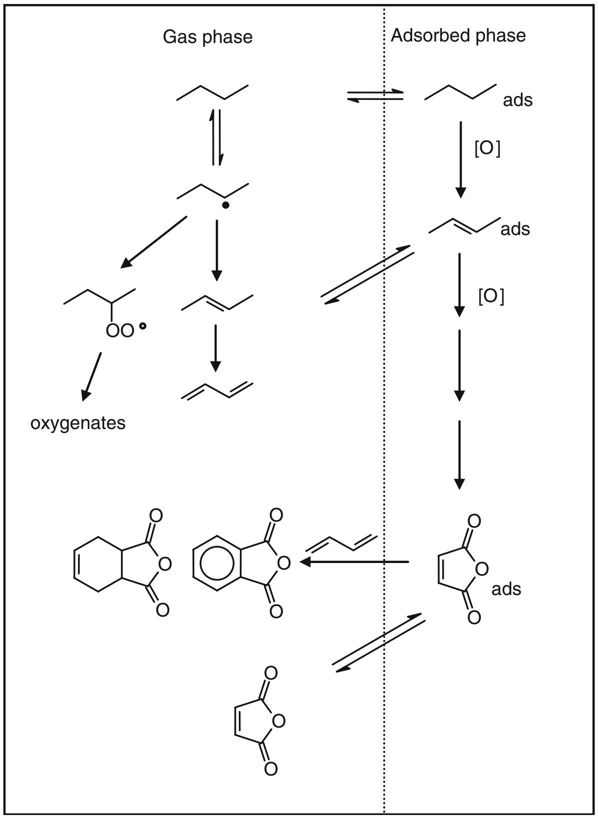

Figure 2. Reaction scheme illustrating the combination of heterogeneous and homogeneous reactions occurring under *n*-butane rich conditions.

Also, homogeneous reactions greatly contribute to *n*-butane conversion with hydrocarbon-rich feed, and affect the nature of the by-products obtained. In order to limit the formation of these by-products, the presence of residual O_2 all along the catalytic bed is necessary. This confirms that a staged feeding of oxygen may be desirable. On the other hand, it is also evident that the VPP is not able to operate under very high *n*-butane-to-oxygen feed ratios; in this case, the doping with suitable elements may be useful to limit the extensive reduction of V^{4+} and V^{5+}. Data published by Ledoux *et al.* on β-SiC-supported VPP [86] suggest that the availability of the oxidant, either as adsorbed oxygen species or as lattice oxygen ion, may be limited due to mass and heat transfer limitations. When conditions develop that favour transfer phenomena, by the use of highly heat-conductive materials, high yield to MA can be obtained even under hydrocarbon-rich conditions, and with O_2 as the limiting reactant.

7. Alternative reactor configurations for O_2 staging: Membrane reactors

The potential advantage in the use of membrane reactors is the separation of the hydrocarbon and oxygen feeds at the two sides of the tubular ceramic membrane, with permeation of oxygen through the membrane and delivery of a controlled amount of it to the catalytic bed. This also makes possible to use overall feed ratios that would be flammable, if the two reactants were fed together [119]. Parameters investigated were the pressure difference across the membrane and the ratio between hydrocarbon and oxygen [120]. Santamaria *et al.* [121–124] studied mesoporous membranes made up of Al_2O_3 tubes impregnated with silica sol or with bohemite to achieve the desired permeation flux of O_2, while avoiding back-permeation of the hydrocarbon; the acidity of the membrane was reduced by impregnation with Li salt. Different reactor configurations were investigated, including Inert Membrane Reactor, in which O_2 permeates inward and the VPO catalyst is packed in the tube side, and Outward Flow IMR, in which the catalyst is packed in the shell side and O_2 flows outwardly. The highest yield to MA claimed was equal to 14%, with 10% *n*-butane total concentration in feed. The work was done in collaboration with Haldor Topsøe, that developed the membrane-based pilot plant.

An interesting phenomenon was reported [125], concerning the positive effect of CO_2 addition on the selectivity and yield to MA. This was first attributed to the more efficient removal of the reaction heat from catalyst surface, due to the superior heat conductive properties of carbon dioxide. Later on the same authors demonstrated that this effect was likely due to an oxidation of the catalytic surface by carbon dioxide, which rendered the VPP more selective; in fact, the phenomenon was more evident under hydrocarbon-rich conditions. The same effect is reported in a recent patent [26].

The reaction can be carried out in an electrochemical membrane reactor, with an oxygen-ion-conducting electrolyte based on YSZ and ScSZ [126]. Also in this case, the advantage lies in the separation of the reactants, fed separately at the opposite side of the membrane; this implies a better control of the heat released, with lower formation of hot-spots [126]. The oxygen flux, the conversion of *n*-butane and the yield of MA were controlled by the externally applied current. However, the selectivity to MA did not exceed 40–42%, carbon oxides being the prevailing products. One drawback of the system was the deactivation of the VPO catalyst, due to the progressive V reduction and to the formation of C deposits.

8. *In-situ* investigation and modelling on the nature of VPP active surface

An excellent discussion of the scientific literature dealing with the working state of the active surface in VPP has been recently published by Schlögl and co-workers [127]. The discussion is supported by *in-situ* measurements of the structure of the active compound and of the composition of the active surface [128,129]. The review also comments on the mechanisms proposed in literature for *n*-butane activation and oxidation to MA. The authors argued that ‘‘the catalytic process requires a substantial flexibility of the reaction centres in their electronic structure,’’ and that ‘‘a rigid and complex structure as existing on the hypothetical basal plane of VPP is not a likely candidate for the required flexibility.’’

The problem of the real nature of the active surface of VPP has been investigated by several authors, often with the use of *in-situ* techniques [130–134]. Many articles discuss the role of different crystalline and/or amorphous compounds in VPO, in the complex transformation of the alkane to MA [7,9–11,30,135,136]. While bulk VPP is in all cases assumed to constitute the core of the active phase, hypotheses formulated differ in regard to the nature of the first atomic layers, those that are in direct contact with the gas phase. It is well known that surface reconstruction, especially in the presence of reactive gases, may substantially alter the surface arrangement of atoms as compared to the bulk. However, due to the difficulties in the characterisation of the catalytically active surface under reaction conditions, the alternative hypothesis either indicate the development of surface amorphous layers which play a direct role in the reaction [137–141], or are based on the crystallographic models of the VPP, assuming that specific planes contribute to the reaction pattern [7,9,22,130,142–147], and that the redox process occurs reversibly between VPP and $VOPO_4$ [131,148].

HRTEM images of basal and prism edges of the VPP made possible the identification of non-crystalline adlayer, about 1 nm thick, on the surface of equilibrated VPO catalysts [127]. By application of *in-situ* X-ray absorption spectroscopy (XAS) and *in-situ* XPS, it was concluded that the working surface is a two-dimensional structure containing more O than that present in the VPP; it is originated *in-situ* by hydrolysis of the VPP, which is metastable under reaction conditions [149]. The authors viewed this surface layer as being constituted of a binary V_xO_y, the growth of which is hindered by phosphate groups [127–129]. This is different from the development of the thick layers of amorphous phases or from segregation of $VOPO_4$, detrimental for catalytic performance, which are more typical of fresh or non-equilibrated catalysts. In contrast with this hypothesis are the results reported by Guliants *et al.* [150]; the authors found, by means of *in-situ* Raman and XRD techniques, that a disordered layer about 2 nm thick, covering the surface (100) planes of fresh VPP, disappeared during equilibration yielding a solid with steady and optimal catalytic performance.

Considerable advancements have also been made in the theoretical description of the nature of active sites in VPP, modelled through computational procedures. Witko *et al.* [151,152] reported about DFT calculations of the electronic structure for different clusters modelling a defective VPP (100) surface. It was found that neutral isolated oxygen vacancies may act as sources for enhancing the activity and selectivity of VPO. Moreover, it was found that triply coordinated oxygen sites (bridging two V atoms and one P atom) are strongly nucleophilic, and can participate in the C–H bond splitting.

The study of the electronic properties of the VPP (100) surface using the cluster model or the periodic treatment, and the DFT method, allowed Hodnett and co-workers [153–156] to conclude that V species act as hydrocarbon chemisorption sites, while nucleophilic terminal P–O oxygen (the most basic surface O according to the authors) perform the selective oxyfunctionalisation of the reactant. Dissociative chemisorption of water may play a role in perpetuation of the oxidation cycle. A computation of the interaction between 1-butene and VPP (100), which was found to be very different from the interaction calculated for *n*-butane, indicated that butene may not be an intermediate in *n*-butane oxidation over VPP.

9. Conclusions

Despite the VPO catalyst for *n*-butane oxidation to MA has been the object of investigation since several years, still the number of papers and patents published on this topic is quite remarkable. The reason for this is that numerous aspects concerning the nature of the active surface, and the role of each catalyst component in the reaction mechanism, yet need to be clarified. The complexity of the VPP and the dynamic evolution of the active surface under reaction conditions constitute serious obstacles to the comprehension of these aspects. However, the acquisition of a better knowledge in this highly challenging field represents the key point for the improvement of VPO catalytic properties, that still are far from being optimal.

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