Available online at www.sciencedirect.com

Catalysis Today 99 (2005) 115–122

www.elsevier.com/locate/cattod

The contribution of homogeneous and non-oxidative side reactions in the performance of vanadyl pyrophosphate, catalyst for the oxidation of *n*-butane to maleic anhydride, under hydrocarbon-rich conditions

N. Ballarini[a,b], F. Cavani[a,b,*], C. Cortelli[a], F. Gasparini[a], A. Mignani[a], F. Pierelli[a], F. Trifirò[a], C. Fumagalli[c], G. Mazzoni[c]

[a]*Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy*
[b]*INSTM, Research Unit of Bologna, Italy*
[c]*Lonzagroup, Via E. Fermi 51, 24020 Scanzorosciate (BG), Italy*

Abstract

The reactivity of vanadyl pyrophosphate, catalyst for the selective oxidation of *n*-butane to maleic anhydride, was examined under *n*-butane-rich conditions, simulating a feed in which oxygen is the limiting reactant, and a process in which the unconverted *n*-butane is recycled. A lower selectivity to maleic anhydride was found with respect to the hydrocarbon-lean conditions, due to the higher selectivity to carbon oxides and to the formation of C_8 by-products: tetrahydrophthalic and phthalic anhydrides. The latter compounds formed by a consecutive reaction of maleic anhydride with the unsaturated C_4 intermediates. This occurred under conditions of total oxygen conversion, due to the decreased catalyst oxidizing property. A relevant contribution of radicalic, homogeneous reactions was also observed, which mainly led to the formation of carbon oxides and olefins. This contribution decreased in the presence of the catalyst, which acted as a radical scavenger, but nevertheless remained important at temperatures higher than 400 °C. When conditions were used under which the conversion of oxygen was not total, olefins generated in the gas phase reacted at the catalyst surface yielding maleic anhydride. This homogeneously initiated heterogeneous process led to an unusual effect, of a relevant increase of maleic anhydride yield over 400 °C.

Keywords: Vanadyl pyrophosphate; Oxidation of *n*-butane; Maleic anhydride; Hydrocarbon-rich conditions; Homogeneous reactions

1. Introduction

One option for the improvement of the performance of chemical processes is the increase of productivity (space–time yield), achieved by increasing the partial pressure of the limiting reactant in feedstock, and by adjusting reaction parameters such as temperature and residence time in order to obtain an acceptable conversion of the reactant [1]. The improvement is possible provided the catalyst is able to sustain high turn-over rates, and the active surface does not saturate due to the higher gas phase concentration of the reactant. A saturation of active sites would imply a decrease of conversion, which might not be compensated by the increase in product concentration at the reactor outlet. This aspect is even more delicate in the case of the selective oxidation of hydrocarbons which operate with a redox mechanism [2], where a suitable balance between (i) oxidizing sites, which are in charge for hydrocarbon transformation, and (ii) reducing sites, those which activate molecular oxygen to replenish the anionic vacancies which develop as a consequence of the O^{2-} insertion on the substrate, establishes. The rates of the two reactions which constitute the redox mechanism depend on the concentration of the oxidized and reduced sites at the catalyst surface. Under steady conditions they are function of (i) the ratio between the hydrocarbon (the reducing agent) and molecular oxygen (the oxidizing agent) in the gas phase, and (ii) the rate of ionic diffusional phenomena in the bulk of the solid, the driving force for which is the development of

---

* Corresponding author. Tel.: +39 051 2093680; fax: +39 051 2093680.
E-mail address: cavani@ms.fci.unibo.it (F. Cavani).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.09.030

concentration gradients of the ions between the surface and the bulk.

One reaction consolidated at an industrial level since many years is the selective oxidation of *n*-butane to maleic anhydride, catalyzed by vanadyl pyrophosphate, $(VO)_2P_2O_7$ [3]. It is carried out with different technologies, i.e., (i) fixed-bed, (ii) fluidized-bed, and (iii) circulating-fluid-bed (CFB) reactors. These differ in the partial pressure of *n*-butane in feed, i.e., lower than 1.8% in the case of fixed-bed, around 4% for the fluidized-bed, and higher than 10% for the CFB. In the case of the fixed-bed, the main problem which is met when high partial pressures of hydrocarbon are used, is the removal of the considerable heat of reaction which develops, which would cause the formation of hot-spots, with the associated problems relative to run-away events. Also, higher hydrocarbon concentrations may render the gaseous mixture flammable. This problem is overcome with the fluidized-bed technology [4], while the CFB process developed by DuPont [5–7] operates in a chemical-loop fashion, by decoupling the two steps of the redox process.

The interest for operation with feedstocks richer in *n*-butane is confirmed by the scientific papers which have recently appeared [8–10]. In general, a poor performance in terms of selectivity to maleic anhydride is reported, attributed to the prevalent formation of carbon oxides. The chemical–physical features of the vanadyl pyrophosphate were found to affect the catalytic performance under hydrocarbon-rich conditions, even more than for the reaction carried out at low concentration of *n*-butane [11]. Options for modifications which, when applied to the vanadyl pyrophosphate, lead to an improvement of the performance under *n*-butane-rich conditions, have been described in works recently published [12–15]. For instance, the dispersion of the vanadyl pyrophosphate over β-SiC, for fixed-bed application, leads to a considerable improvement of the maximum yield to maleic anhydride with respect to the unsupported active phase [13].

In the present work, we describe the reactivity of a well-crystallized vanadyl pyrophosphate, obtained by ageing the catalyst in a pilot-plant reactor for several hundred hours, when *n*-butane concentrations at the reactor inlet between 1.7 and 10 mol% are used. A special attention is given to the contribution of homogeneous reactions and to the formation of by-products other than maleic anhydride and carbon oxides. These aspects are often neglected in papers dealing with the reactivity under *n*-butane-rich conditions.

2. Experimental

The catalyst precursor, $VOHPO_4 \cdot 0.5H_2O$, was prepared by the "organic procedure", using isobutanol and benzyl alcohol as the reducing agent for V_2O_5 in the presence of H_3PO_4. The precipitate was filtered, washed with isobutanol and dried at 125 °C overnight. After a spray-drying conglomeration of particles into fluidizable material, the compound was thermally treated to develop the vanadyl pyrophosphate, and then the reaction was run in fluidized-bed pilot reactor for 2 months. This procedure led to the development of a fully equilibrated catalyst, and all the standard characterization techniques evidenced the presence of crystalline vanadyl pyrophosphate. Catalytic tests were then carried out in a laboratory glass flow-reactor, loading 3 g of the equilibrated catalyst, diluted with inert material. The products were analyzed by means of gas chromatography. A HP-1 column was used for the separation of C_4 hydrocarbons, acetic acid, acrylic acid, maleic anhydride, tetrahydrophthalic anhydride, phthalic anhydride. A Carbosieve SII column was used for the separation of oxygen, carbon monoxide and carbon dioxide.

3. Results and discussion

3.1. The reactivity under n-butane-rich conditions, with total conversion of oxygen

Figs. 1 and 2 compare the catalytic performance under *n*-butane lean conditions (which in our lab reactor are run using 1.7% *n*-butane and 17% oxygen in feed), and under hydrocarbon-rich conditions, respectively. In the latter case, the concentration of oxygen at the reactor inlet was 17%, while that of the hydrocarbon was 10 mol%. It is worth mentioning that the latter feed composition is flammable, and therefore operation with such feed should be conveniently operated, at an industrial level, with a fluidized-bed reactor, and by mixing the recycle feed (with the desired amount of inert in it), and make-up reactants separately, directly inside the catalytic bed. On the other hand, with such a feed composition, operation can be conveniently conducted so to keep the oxygen concentration at the reactor outlet well below the MOC (maximum oxygen concentration). Therefore, the feed composition here employed might simulate the reactor inlet for a process in which (i) oxygen is the limiting reactant, (ii) per pass *n*-butane conversion is a function of the distribution of

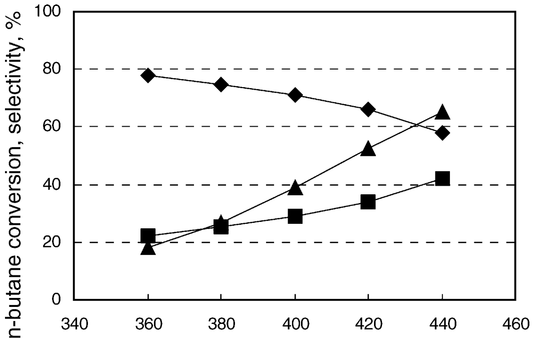

Fig. 1. Conversion of *n*-butane (▲), selectivity to maleic anhydride (◆) and to CO + CO_2 (■), as functions of temperature. Feed composition: 1.7 mol% *n*-butane, 17% oxygen, remainder He. W/F = 1.3 g s cm^{-3}.

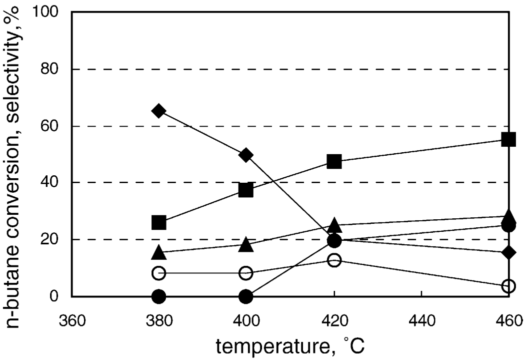

Fig. 2. Conversion of *n*-butane (▲), selectivity to maleic anhydride (◆), $CO + CO_2$ (■), acrylic + acetic acids (○), and tetrahydrophthalic + phthalic anhydrides (●), as functions of temperature. Feed composition: 10 mol% *n*-butane, 17% O_2, remainder He. W/F = 1.3 g s cm^{-3}.

products (the formation of which involves different stoichiometries as regards oxygen consumption), and (iii) a relevant concentration of inert is maintained in the recycle loop.

Data of Figs. 1 and 2 show remarkable differences between the two conditions. The conversion of *n*-butane under hydrocarbon-rich conditions was lower than that obtained under leaner conditions, especially at above 400 °C (see also considerations concerning the productivity, discussed in relation to data of Fig. 4); the conversion of oxygen was total at 460 °C. Under rich conditions, the increase of *n*-butane conversion from 380 to 460 °C was relatively small (from 15 to 30%). This may be attributed either (i) to a variation of the apparent activation energy (possibly coming from a contribution of intra-particle or inter-particle diffusional limitations to the rate-limiting step), or (ii) to a change in the nature of the rate-limiting step when the gas-phase composition is modified, or (iii) to a relevant contribution of homogeneous reactions, which typically differ from heterogeneous phenomena in regards to variations with temperature. This aspect is further discussed in Section 3.3.

The most important difference between the two feed compositions, however, concerned the distribution of products. Under hydrocarbon-lean conditions (Fig. 1), the products obtained were maleic anhydride, CO and CO_2. Only traces of acrylic acid and acetic acid formed, with selectivity lower than 1%, and there was no formation of heavier by-products. As usual, the selectivity to maleic anhydride declined for increasing reaction temperatures, while that to CO_x correspondingly increased. Under hydrocarbon-rich conditions, at 380 °C the selectivity to maleic anhydride was lower than that obtained under leaner conditions for the same temperature, mainly because of the relevant formation of acrylic and acetic acid, the overall selectivity of which was around 10%. The formation of the latter products remained constant when the reaction temperature was increased, while the selectivity to maleic anhydride rapidly fell. This was due to the increased selectivity to carbon oxides, and, even more remarkably, to the formation of two C_8 compounds, tetrahydrophthalic anhydride and phthalic anhydride.

The formation of phthalic anhydride is also relevant when the vanadyl pyrophosphate is used as the catalyst for the oxidation of *n*-pentane [16,17]. This was attributed to an acid-type condensation and dehydrocyclization between two unsaturated C_5 hydrocarbons, leading to the formation of a C_{10} alkylaromatic, which is the precursor of the C_8 anhydride. Thus, the well-known surface Lewis acidity of the vanadyl pyrophosphate contributes to catalyze the formation of condensation products. The two main products of selective oxidation, maleic and phthalic anhydrides, formed by parallel reactions from *n*-pentane.

The formation of heavy by-products is not observed in the oxidation of *n*-butane under hydrocarbon-lean conditions, due to the fact that an acid-catalyzed dimerization and dehydrocyclization of two C_4 olefins would not lead to the formation of a cyclic aliphatic hydrocarbon having two adjacent methyl groups (the possible precursor for the formation of *o*-xylene and then of phthalic anhydride), but rather to a compound which, when aromatized, would lead to *p*-xylene [16]; if formed, this would finally be oxidized to carbon oxides and to maleic anhydride [18]. Therefore, under the hydrocarbon-rich conditions used in the present work, the formation of phthalic anhydride through an acid-catalyzed mechanism is not likely. Moreover, this mechanism does not include the formation of tetrahydrophthalic anhydride, which instead is one important product from *n*-butane under rich conditions.

Another possible mechanism for the formation of the C_8 by-products may consist in a cyclo-addition of intermediate butadiene to maleic anhydride (Diels–Alder reaction), with formation of tetrahydrophthalic anhydride. Even though thermodynamically less favoured at high temperature, this reaction might be shifted towards the formation of the product by the consecutive, irreversible oxidative transformation of tetrahydrophthalic anhydride to phthalic anhydride. This mechanism is supported by tests shown in Fig. 3,

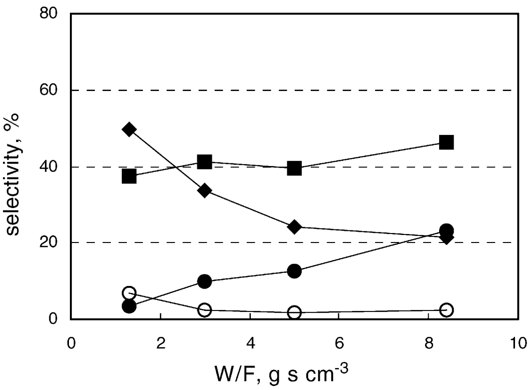

Fig. 3. Selectivity to maleic anhydride (◆), $CO + CO_2$ (■), acrylic + acetic acids (○), and tetrahydrophthalic + phthalic anhydrides (●), as functions of residence time. Feed composition: 10% *n*-butane, 17% O_2, remainder He; temperature 400 °C.

made at increasing residence times. Results evidence that: (i) tetrahydrophthalic and phthalic anhydrides are secondary products (while maleic anhydride is a primary product), and (ii) the increase of selectivity to C_8 compounds corresponds to a decrease in the formation of maleic anhydride.

Whichever is the mechanism for the formation of the C_8 by-products, either (i) an acid-catalyzed dimerization and dehydrocyclization of intermediate C_4 olefins, followed by aromatization and oxidation, or (ii) a reaction between C_4 diolefin and maleic anhydride, it is clear that the growing selectivity to these by-products, for increasing reaction temperatures, is due to a decreased ability of the catalyst to give O-insertion on the intermediate unsaturated C_4 compounds. Under conditions of total O_2 conversion, instead of being oxidized to maleic anhydride, these intermediates undergo other transformations in the fraction of catalytic bed which is exposed to the anaerobic condition. This fraction of the bed increases when the reaction temperature is raised.

The performance of the vanadyl pyrophosphate at high *n*-butane partial pressure was first studied many years ago [19], and it was established that one important factor, in order to make the multi-step transformation of the alkane to maleic anhydride feasible, is the surface availability of O-insertion sites. Specifically, it was found that at relatively 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 the latter into the gas phase; this leads to a lower selectivity to maleic anhydride. The O-insertion properties are also a function of the vanadyl pyrophosphate morphology, and it is known that the preferential exposure of peculiar crystallographic planes may lead to higher activity and/or selectivity to maleic anhydride. This is confirmed by results of Kamiya et al. [11], who found that the rose-petals morphology, with a compound exhibiting the preferential exposure of the (2 0 0) plane, was the most active catalyst at 5% *n*-butane concentration, as a consequence of an higher vanadium reducibility and reoxidizability. Differences between catalysts were much smaller at low *n*-butane concentration.

The paper by Mallada et al. [10] points out that the performance of the vanadyl pyrophosphate under "oxidizing" (2% *n*-butane and 20% oxygen) and "reducing" (10% *n*-butane, 15% oxygen) conditions is very different. Specifically, under reducing conditions the catalyst gave a lower hydrocarbon conversion (but the productivity was higher), and a lower selectivity to maleic anhydride. The effect was attributed to the development of a defective vanadyl pyrophosphate, as a consequence of the introduction of planar shear defects generated by the loss of lattice oxygen, and to the formation of V^{3+} species. While in proximity of the reactor entrance, where oxygen was still available, the characteristics of the vanadyl pyrophosphate were comparable under oxidizing and reducing conditions, in the latter case and in the presence of decreasing concentrations of oxygen along the reactor, a reduced vanadyl pyrophosphate developed. The latter not only was substantially unable to convert *n*-butane to maleic anhydride, but also was responsible for the combustion of maleic anhydride formed in the uppermost, oxidized catalyst layers.

Mota et al. [8,9] found that the progressive reduction of the vanadyl pyrophosphate under *n*-butane-rich conditions (16.6% *n*-butane and 10% oxygen) led to an increase of hydrocarbon conversion and to a drastic fall of selectivity to maleic anhydride. Also in this case, the behavior was attributed to the development of a reduced catalyst surface and to the formation of C deposits. The need was pointed out for available O-insertion sites, and for an optimal V^{5+}/V^{4+} ratio, in order to obtain the transformation of all reaction intermediates to maleic anhydride. It was also found that the doping of the vanadyl pyrophosphate with either Co or Mo favoured the development of a higher V^{5+}/V^{4+} ratio under *n*-butane-rich conditions, and limited the formation of C deposits [20].

Therefore, there is a general agreement that a strong reduction of the vanadyl pyrophosphate is the reason for the bad performance under hydrocarbon-rich conditions. The main difference between the present work and results reported by other groups concerns the nature of the by-products which are responsible for the lower selectivity to maleic anhydride. We demonstrate here that due to the lower amount of O-insertion sites, a fraction of intermediate olefinic compounds reacts preferentially with the already formed maleic anhydride, giving rise to the formation of the C_8 by-products, and lowering the selectivity to maleic anhydride.

Fig. 4 plots the value of the overall rate of *n*-butane transformation, measured at 380 °C (that is under conditions of low *n*-butane conversion), and the selectivity to maleic anhydride at 15 and 40–50% hydrocarbon conversion, as functions of the *n*-butane concentration in feed. Phthalic and tetrahydrophthalic anhydrides formed only in tests carried out with 10% *n*-butane in feed. Other effects were the following:

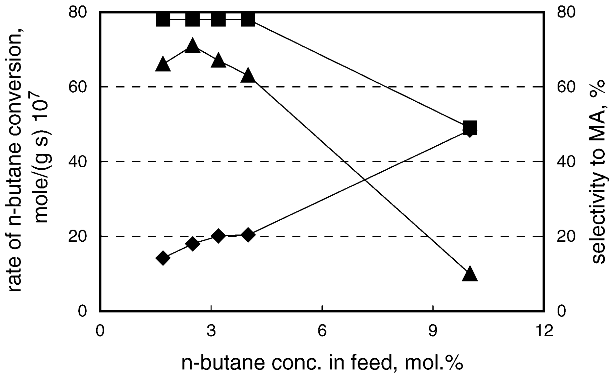

Fig. 4. Effect of *n*-butane concentration in feed on the rate of *n*-butane conversion at 380 °C (◆), and on the selectivity to maleic anhydride at 15% *n*-butane conversion (■), and at 40–50% *n*-butane conversion (▲). W/F 1.3 g s cm^{-3}.

(a) The rate of *n*-butane transformation reached a plateau at 4% hydrocarbon concentration in feed, suggesting a surface saturation effect. However, the rate measured at 10% hydrocarbon was much higher than that one at lower *n*-butane concentrations. This is strongly in favour of a contribution from a homogeneous *n*-butane transformation, which overlaps to the heterogeneous mechanism at high *n*-butane concentration.
(b) At low conversion, the selectivity to maleic anhydride was not affected by the hydrocarbon concentration in feed, when the latter was between 1.3 and 4 mol%; the decrease of selectivity at 10% *n*-butane was mainly due to the higher formation of acrylic acid, acetic acid and carbon oxides.
(c) At high conversion, instead, the selectivity to maleic anhydride already began to decline at 2.5% *n*-butane in feed, due to the higher formation of carbon oxides, and became very low at 10% hydrocarbon concentration. In the latter case, the low selectivity was mainly due to the formation of carbon oxides and to the consecutive reactions occurring upon maleic anhydride, yielding tetrahydrophthalic and phthalic anhydrides.

3.2. The reactivity under n-butane-rich conditions, with incomplete conversion of oxygen

Results plotted in Figs. 2–4 indicate that under reducing conditions, and specifically under conditions of total oxygen conversion, two phenomena affect the catalytic performance: (i) consecutive reactions upon maleic anhydride lead to the formation of C_8 by-products, and (ii) homogeneous reactions contribute to *n*-butane conversion.

In order to confirm the role of oxygen on the distribution of products, *n*-butane-rich tests were carried out using higher oxygen concentration in feed. Fig. 5 plots the effect of temperature on catalytic performance at 10% *n*-butane and 25% oxygen in feed. Under such conditions, the conversion of oxygen was not total (at 460 °C, it was equal to 75%). The main differences with respect to data reported in Fig. 2 are:

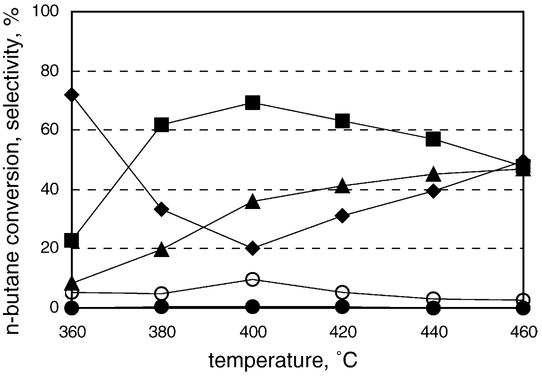

Fig. 5. Conversion of *n*-butane (▲), selectivity to maleic anhydride (◆), CO + CO_2 (■), acrylic acid + acetic acid (○), and tetrahydrophthalic + phthalic anhydrides (●), as functions of temperature. Feed composition: 10 mol% *n*-butane, 25% O_2, remainder He. W/F = 1.3 g s cm^{-3}.

(a) A higher conversion of *n*-butane.
(b) A considerable decrease in the formation of C_8 by-products, the selectivity of which was now not higher than 0.5 %. The selectivity to acrylic + acetic acid instead was the same as that obtained with lower oxygen concentration (Fig. 2). Therefore, when molecular oxygen is available along the entire catalytic bed, the rate of intermediate C_4 olefins oxidation to maleic anhydride becomes quicker than the rate of reaction with maleic anhydride itself to yield the C_8 by-products. This confirms the importance of having a suitable number of O-insertion sites on the catalyst surface, in order to have a rapid transformation of the intermediates to maleic anhydride.
(c) A quite unexpected effect was the minimum in the selectivity to maleic anhydride, at 400 °C; in fact, at above 400 °C, the selectivity to maleic anhydride increased, reaching the 50% at 460 °C, for a *n*-butane conversion equal to 46%. This gives the best yield to maleic anhydride (23%) ever reported in literature for operation under *n*-butane-rich conditions, with an unsupported VPO catalyst (55% yield is claimed by Ledoux et al. [13] for β-SiC-supported VPO, under conditions similar to those employed in the present work). The effect was completely reversible and reproducible, when tests were repeated by changing the reaction temperature from low to high, and vice-versa, and when shifting the gas-phase composition from hydrocarbon-rich to hydrocarbon-lean. This also indicates that coke accumulation, likely occurring under *n*-butane-rich conditions [8,21] did not cause a significant catalyst deactivation, and a lack of reproducibility in catalytic tests when the reaction conditions were changed.

The effect observed, of a minimum in the selectivity to maleic anhydride, can be attributed to a change in the reaction mechanism occurring at high temperature. It is worth reminding that this phenomenon occurred in the presence of (i) unconverted oxygen in the gas-phase, and (ii) high concentration of *n*-butane in feed. On the contrary, the effect was not observed under hydrocarbon-lean conditions (Fig. 1), or under hydrocarbon-rich conditions with total oxygen conversion (Fig. 2). Therefore, it is possible that an additional contribution to the formation of maleic anhydride derives from the oxidation of C_4 unsaturated intermediates, the latter having been generated by the homogeneous reactions. This point is further investigated in the following chapter.

3.3. The contribution of homogeneous reactions

Results obtained clearly indicate that at high *n*-butane concentration the contribution of homogeneous reactions is

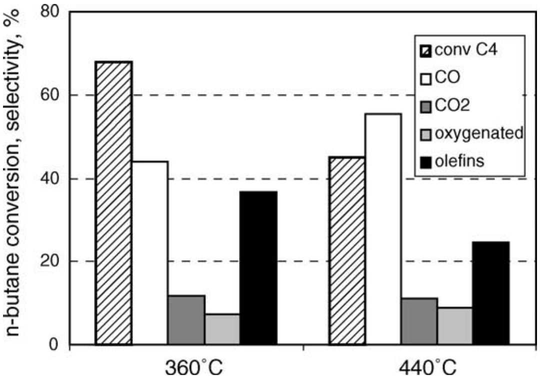

Fig. 6. Conversion of *n*-butane and selectivity to the products as functions of temperature for tests carried out in the absence of catalyst. Feed composition: 10% *n*-butane, 25% O_2, remainder He.

likely. In order to confirm the role of gas-phase reactions, tests have been carried out by feeding the reactant mixture containing 10% *n*-butane and 25% oxygen, either to the empty reactor, or to the reactor filled with inert material (steatite), while keeping the same flow rate as for tests carried out in the presence of the catalyst. Fig. 6 summarizes the results obtained.

At 360 °C the conversion of *n*-butane was close to 70%, that is considerably higher than that achieved in the presence of the catalyst under the same reaction conditions. This means that at relatively low temperature the catalyst is able to suppress, at least in part, the radicalic chain reaction which is initiated in the gas phase. The same quenching effect was not observed when the reactor was filled with inert material, in place of the catalyst. Therefore, the ability of the catalyst to interrupt the chain mechanism is related to the property of active sites to adsorb the radicalic species, and transform them to non-radicalic products (e.g., carbon oxides).

The homogeneous conversion of *n*-butane drastically decreased when the inlet concentration of oxygen was lowered, or when the reaction temperature was increased (*T* 440 °C as compared to 360 °C, in Fig. 6). This is also typical of homogeneous, radicalic-type processes, since the reversible reaction:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

is thermodynamically less favoured at high temperature [1]. This also may explain why in Fig. 5 the conversion of *n*-butane reaches a plateau, despite the availability of oxygen in the gas phase.

Fig. 6 also reports the distribution of products: mainly CO_x (especially CO) and olefins (butenes and butadiene), with minor formation of acrylic acid, acetic acid, crotonaldehyde and methylvinylketone (all included in the term: oxygenated products). These are the products typically obtained, together with maleic anhydride, in the oxidation of butenes catalyzed by vanadyl pyrophosphate [22].

The formation of the olefins occurs either via the mechanism:

$$CH_3{-}CH_2{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH_2{-}CH^{\bullet}{-}CH_3$$

$$CH_3{-}CH_2{-}CH^{\bullet}{-}CH_3 + O_2 \rightarrow CH_3{-}CH{=}CH{-}CH_3 + HO_2^{\bullet}$$

or by dehydrogenation, especially under conditions of low residual oxygen concentration. The distribution of products was not greatly affected by temperature, in the range examined. No maleic anhydride formed.

The presence of the homogeneous reactions explains the phenomena observed in the presence of the catalyst, under hydrocarbon-rich conditions:

(a) The rate of *n*-butane transformation at 10% hydrocarbon in feed, higher than the expected one (Fig. 4).
(b) The formation of acrylic acid and acetic acid (Fig. 2), which in part may derive from the reaction of radicalic fragments with oxygen, either in the gas phase or at the catalyst surface.
(c) The formation of C_8 by-products at temperature higher than 400 °C (Fig. 2), by reaction between olefins, generated in the gas phase at high temperature, and maleic anhydride, generated at the catalyst surface. This reaction is relevant under hydrocarbon-rich conditions only when the oxygen in the gas phase is totally consumed (Fig. 2). Excess oxygen, instead, leads to the disappearance of C_8 by-products (Fig. 5), and to the increase in the formation of maleic anhydride; therefore, under these conditions the olefins generated in the gas phase may react with the oxidizing sites at the catalyst surface, yielding maleic anhydride. This mechanism overlaps to the heterogeneous one, which instead leads to the formation of maleic anhydride with a decreasing selectivity for increasing reaction temperatures. The combination of the two effects generates the minimum in selectivity to maleic anhydride (Fig. 5). Since the selectivity to olefins in the presence of the vanadyl pyrophosphate is very low (traces of olefins were obtained at high temperature only for tests carried out with 10% *n*-butane and 17% oxygen), this further confirms that the olefins produced are transformed by reaction with the catalyst.

The scheme of reaction under hydrocarbon-rich conditions, including both homogeneous and heterogeneous reactions, is summarized in Fig. 7. The relative contribution of the two reactions at temperatures higher than 400 °C, leading either to the formation of the C_8 by-products, or to maleic anhydride, is a function of the oxygen concentration in the gas phase. Strongly reducing conditions, due to the total oxygen consumption, lead to the preferred formation of the C_8 by-products, by reaction between unsaturated C_4 compounds and maleic anhydride (formed in the uppermost fraction of the catalytic bed, where oxygen is still present),

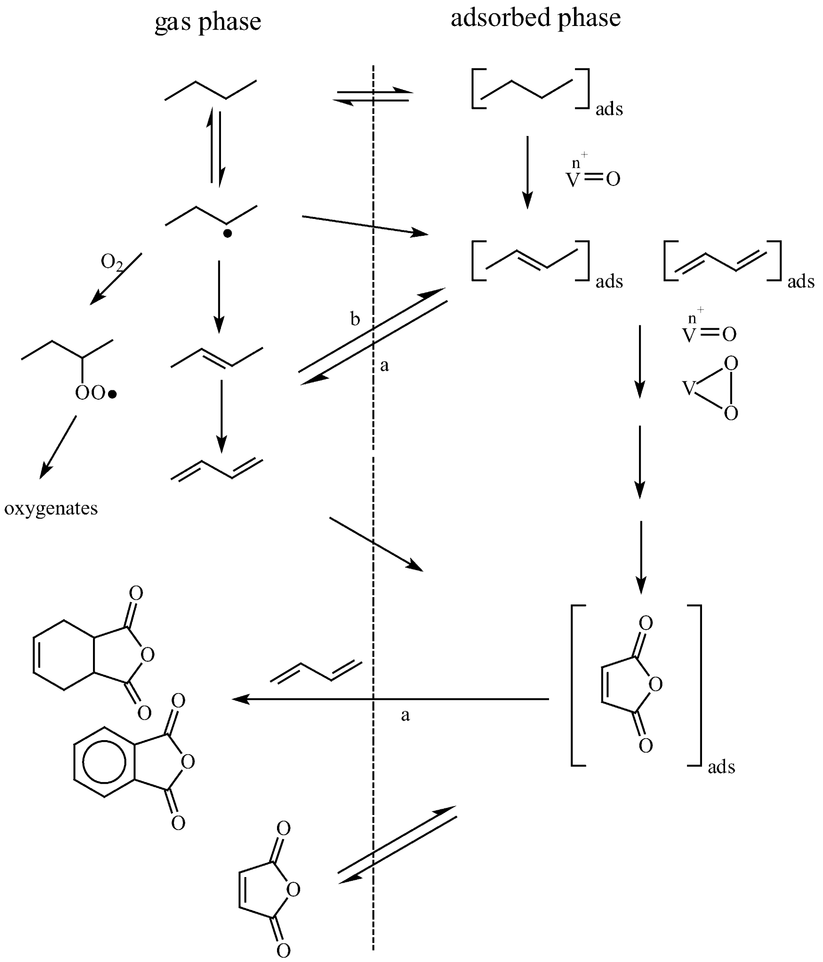

Fig. 7. Reaction scheme for *n*-butane oxidation catalyzed by vanadyl pyrophosphate under hydrocarbon-rich conditions. (a) Pathway preferred under conditions of total oxygen conversion. (b) Pathway preferred under conditions of incomplete oxygen conversion.

either because the number of oxidizing V^{5+} sites is too low [8–10,23], or because the oxidation of butenes to maleic anhydride involves adsorbed O species [24,25], the formation of which requires the presence of gas-phase O_2. Olefins are generated by both the heterogeneous and the high-temperature, homogeneous mechanism. In the presence of excess molecular oxygen, instead, the reaction pathway leading to the transformation of olefins to maleic anhydride is kinetically preferred.

4. Conclusions

The oxidation of *n*-butane to maleic anhydride, catalyzed by vanadyl pyrophosphate, was studied under hydrocarbon-rich conditions, simulating a feed in which molecular oxygen is the limiting reactant. Under these conditions, the selectivity to maleic anhydride was considerably lower than under *n*-butane-lean conditions; above 400 °C, this was due to the higher selectivity to carbon oxides, and to the formation of tetrahydrophthalic and phthalic anhydrides. The latter compounds formed by consecutive Diels–Alder reaction of maleic anhydride with intermediate butadiene; however, this reaction became relevant only under conditions of total oxygen conversion.

The contribution of homogeneous reactions was non-negligible over the entire range of temperature examined, and became important above 400 °C. Under conditions of incomplete conversion of oxygen, the selectivity to maleic anhydride increased when the temperature was raised above 400 °C; this has been attributed to the heterogeneous oxidation of the C_4 olefins' generated in the gas phase by homogeneous reactions.

References

[1] P. Arpentinier, F. Cavani, F. Trifirò, The Technology of Catalytic Oxidations, Technip, Paris, 2001.
[2] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (1954) 41.
[3] G. Centi, F. Cavani, F. Trifirò, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic Publishers/Plenum Press, New York, 2001.
[4] S. Albonetti, F. Budi, F. Cavani, S. Ligi, G. Mazzoni, F. Pierelli, F. Trifirò, Stud. Surf. Sci. Catal. 136 (2001) 141.

[5] R.M. Contractor, H.E. Bergna, H.S. Horowitz, C.M. Blackstone, B. Malone, C.C. Torardi, B. Griffiths, U. Chowdry, A.W. Sleight, Catal. Today 1 (1987) 49.
[6] R.M. Contractor, A.W. Sleight, Catal. Today 1 (1987) 587.
[7] E. Bordes, R.M. Contractor, Top. Catal. 3 (1996) 365.
[8] S. Mota, M. Abon, J.C. Volta, J.A. Dalmon, J. Catal. 193 (2000) 308.
[9] S. Mota, J.C. Volta, G. Vorbeck, J.A. Dalmon, J. Catal. 193 (2000) 319.
[10] R. Mallada, S. Sajip, C.J. Kiely, M. Menendez, J. Santamaria, J. Catal. 196 (2000) 1.
[11] Y. Kamiya, E. Nishikawa, T. Okuhara, T. Hattori, Appl. Catal. A: Gen. 206 (2001) 103.
[12] G.J. Hutchings, R. Higgins, Appl. Catal. A: Gen. 154 (1997) 103.
[13] M.J. Ledoux, C. Crouzet, C. Pham-Huu, V. Turines, K. Kourtakis, P.L. Mills, J.J. Leoru, J. Catal. 203 (2001) 495.
[14] O. Rubio, R. Mallada, J. Herguido, M. Menendez, Ind. Eng. Chem. Res. 41 (2002) 5181.
[15] Y. Kamiya, E. Nishikawa, A. Satsuma, T. Okuhara, Bull. Chem. Soc. Jpn. 76 (2003) 837.
[16] F. Cavani, A. Colombo, F. Giuntoli, E. Gobbi, F. Trifirò, P. Vazquez, Catal. Today 32 (1996) 125.
[17] M. Lopez Granados, J.M. Coronado, J.L.G. Fierro, F. Cavani, F. Giuntoli, F. Trifirò, Surf. Interf. Anal. 25 (1997) 667.
[18] F. Cavani, F. Trifirò, Appl. Catal. A: Gen. 157 (1997) 195.
[19] G. Centi, G. Fornasari, F. Trifirò, J. Catal. 89 (1984) 44.
[20] M. Abon, J.M. Herrmann, J.C. Volta, Catal. Today 71 (2001) 121.
[21] M.J. Lorences, G.S. Patience, F.V. Diez, J. Coca, Appl. Catal. A 263 (2004) 193.
[22] F. Cavani, G. Centi, I. Manenti, A. Riva, F. Trifirò, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 585.
[23] U. Rodemerck, B. Kubias, H.-W. Zanthoff, G.-U. Wolf, M. Baerns, Appl. Catal. A: Gen. 153 (1997) 217.
[24] B. Schiøtt, K.A. Jørgensen, Catal. Today 16 (1993) 79.
[25] D. Wang, M.A. Barteau, Catal. Lett. 90 (2003) 7.