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Catalysis Today 32 (1996) 125-132

CATALYSIS TODAY

Role of surface properties of the vanadyl pyrophosphate in the formation of maleic and phthalic anhydrides by *n*-pentane oxidation

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Abstract

The mechanism of synthesis of maleic and phthalic anhydrides by the gas phase oxidation of *n*-pentane over VPO-based catalysts was studied. The oxidation of the paraffin was carried out under conditions which may lead to the isolation of possible reaction intermediates: very low residence time and high *n*-pentane/oxygen ratio. Under these conditions a number of by-products were identified, which were attributed to the oxidation of intermediate pentene and pentadiene, as well as other products with more than 5 C atoms, among which were alkylaromatics. Alkylaromatics also were found to be formed in the anaerobic transformation of pentadiene. A mechanism is proposed, which takes into account the oxidehydrogenation of the paraffin to pentene and pentadiene, followed by two parallel pathways: (i) dimerization, dehydrocyclization and aromatization of the diolefin, followed by oxidation of the alkylaromatic to phthalic anhydride, and (ii) multi-step oxidation of pentadiene to maleic anhydride.

Keywords: Surface properties; Vanadyl pyrophosphate; Maleic anhydride; Phthalic anhydride; *n*-Pentane oxidation

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1. Introduction

The synthesis of maleic anhydride on an industrial scale is carried out by oxidation of *n*-butane, catalyzed by mixed oxides of vanadium and phosphorus [1]. The active phase in the selective transformation of the paraffin to the anhydride is vanadyl pyrophosphate, $(VO)_2P_2O_7$. Vanadyl pyrophosphate has also been found to be active in the transformation of *n*-pentane to maleic and phthalic anhydrides [2-6]. The catalytic performance in this reaction is affected by the extent of crystallinity of the vanadyl pyrophosphate, as well as by the presence of $VOPO_4$ phases [3]. The formation of a C_8 compound, phthalic anhydride, starting from the C_5 reactant, illustrates the ability of the catalyst to upgrade the paraffin. The mechanism of formation of anhydrides from *n*-pentane has not yet been established, in part due to the absence of any further product (besides the maleic and phthalic anhydrides and the carbon oxides) which might be helpful in obtaining information on the reaction pathway. In this respect, the reaction is comparable to the well-known *n*-butane oxidation, which only yields maleic anhydride and carbon oxides. Golinelli and Gleaves [5], even at milliseconds residence time in a TAP reactor, could only detect methylfuran and furan as possible reaction intermedi-

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PII S0920-5861(96)00085-5

ates in the synthesis of maleic anhydride from *n*-pentane. Different mechanisms for the pathway leading to the formation of phthalic anhydride have been proposed, but only indirect evidence could be provided. For instance, Centi et al. [7,8] proposed the formation of intermediate cyclopentadiene and its dimerization to yield a bicyclo adduct, precursor of the phthalic anhydride formation, even though other possible mechanisms could not be excluded. On the basis of FT-IR spectra of adsorbed species, it has been suggested that the C–C bond formation could occur by a surface template reaction between pentadiene and 5-methyloxocyclobut-3-en-2-one [9]. Surface template reactions, formally analogous to Diels–Alder condensations, might occur on the catalyst surface, but should be even more favourably expected by reaction between maleic anhydride and pentadiene. On the contrary, no correlation exists between the formation of maleic anhydride and that of phthalic anhydride [3]. In addition, the same reaction should occur between adsorbed butadiene and the unsaturated lactone (or maleic anhydride) in the case of *n*-butane oxidation; on the contrary, phthalic anhydride is obtained only in traces from *n*-butane.

The aim of the present research was to obtain a better understanding of the mechanism of *n*-pentane oxidation to maleic and phthalic anhydrides. The reaction was studied under 'extreme' conditions, very low residence time and high hydrocarbon-to-oxygen ratio, in order to isolate possible reaction intermediates. The acid properties of the catalyst, which may play a role in the mechanism, also were investigated. Finally, the reactivity of possible reaction intermediates, such as pentene and pentadiene (both under aerobic and anaerobic conditions), as well as of alkylaromatics, was studied.

2. Experimental

The catalyst was prepared following the anhydrous procedure, based on reduction of V_2O_5 in an alcohol medium in the presence of H_3PO_4 [1]. The compound obtained, $VOHPO_4 \cdot 0.5H_2O$, was dehydrated and calcined under a nitrogen atmosphere up to 723 K. The compound was then aged in an *n*-pentane/air mixture at 613 K for 500 h. The equilibrated catalyst is characterized by the presence of only well crystallized $(VO)_2P_2O_7$. The oxidation reactions were carried out in a tubular flow reactor operating at atmospheric pressure. Details concerning the apparatus and the analysis of the products have been given elsewhere [2]. Catalytic tests of benzene alkylation with propylene were carried out in a batch autoclave reactor, at 30 atm of pressure, temperature 493 K, and benzene-to-propylene molar ratio 1/7. Details about the product analysis and catalyst preparation have been given elsewhere [10].

3. Results and discussion

3.1. Reactivity of *n*-pentane

Fig. 1a and Fig. 1b show the product distributions in the oxidation of 1% *n*-pentane in air at 613 K as a function of residence time (expressed as the ratio between catalyst weight and volumetric flow rate, W/F). The main products obtained were maleic anhydride, phthalic anhydride and carbon oxides. Traces were also found of other by-products (whose selectivity was however lower than 1.2%), amongst which the most relevant were cinnamaldehyde (3-phenylpropenal), citraconic anhydride (methylmaleic anhydride) and 2H-pyran-2-one; above $W/F = 1$ g s/ml these by-products were not formed at all. Fig. 1a shows that the selectivity to the main products was practically constant over the entire range examined. This indicates that all of them are primary products, and that under these conditions no consecutive reactions of oxidative degradation occur. Therefore, these data do not allow us to correlate any of the by-products identified to the formation of maleic and phthalic anhydrides, even though the presence of

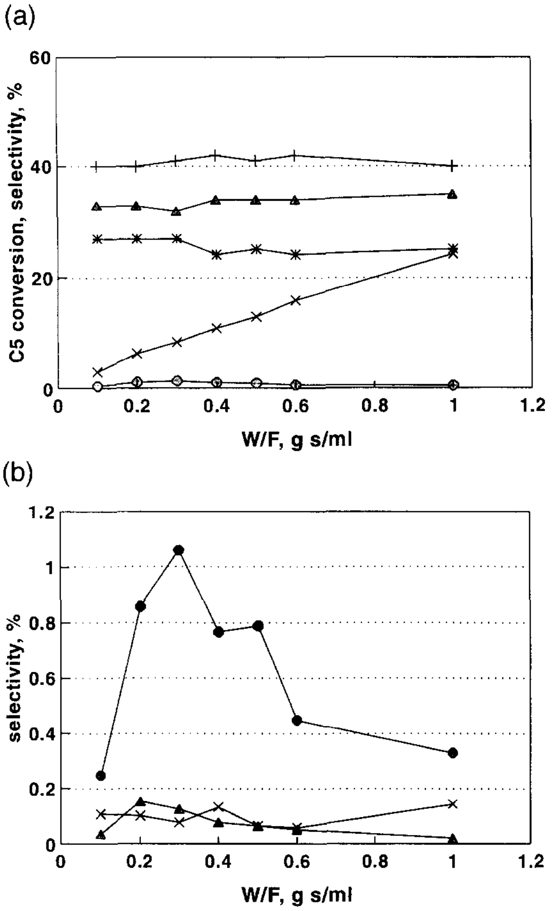


Fig. 1. (a) n-Pentane conversion (×) and selectivity to maleic anhydride (△), phthalic anhydride (+), carbon oxides (∗) and other by-products (○) as functions of residence time (W/F ratio). (b) Selectivity to the main by-products as functions of residence time (W/F ratio): 2H-pyran-2-one (○), citraconic anhydride (×) and cinnamaldehyde (△). Conditions: T, 613 K; feedstock, 1 mol% n-pentane in air; catalyst amount, 3 g.

these by-products clearly indicates the formation of intermediate unsaturated C_5 and C_{5+} compounds. The citraconic anhydride also shows a non-negligible selectivity when the conversion is extrapolated to nil conversion, indicating that this compound is also a primary product, likely formed by oxidation of isopentane, present in traces in the feedstock. Cinnamaldehyde and 2H-pyran-2-one, instead, are clearly formed by consecutive reactions from other intermediate products, probably pentene and pentadiene. It is worth mentioning that a careful analysis of the n-pentane reactant allowed us to exclude the presence of olefinic impurities in the feedstock, even in traces.

Fig. 2a and Fig. 2b report the productivity to the various products obtained when the hydrocarbon content in the feed was increased from 1 to 20 mol%, at 613 K and $W/F = 1$ g s/ml. In all cases the hydrocarbon was diluted in air, and therefore the oxygen content in the feed varied from 20 mol% at low hydrocarbon concentration to 16 mol% at higher n-pentane concentration (20 mol%). Nevertheless, the conversion was never limited by a lack of oxygen; large

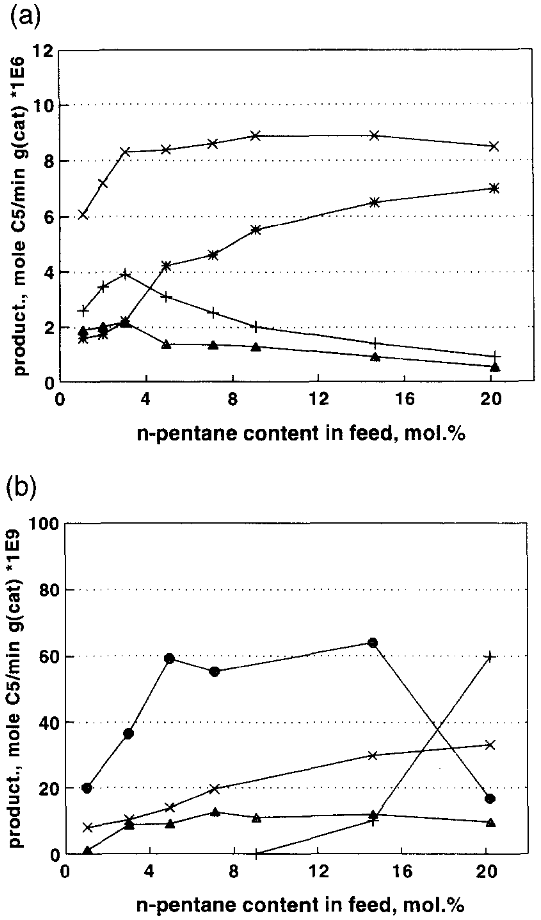


Fig. 2. (a) Rate of n-pentane depletion (×), and productivity to maleic anhydride (△), phthalic anhydride (+) and carbon oxides (∗) as functions of the n-pentane content in the feed. (b) Productivity of 2H-pyran-2-one (○), citraconic anhydride (×), cinnamaldehyde (△) and acrylic acid (+) as functions of the n-pentane content in the feed. Conditions: T, 613 K; W/F, 1 g s/ml; catalyst amount, 3 g.

amounts of unconverted oxygen were found at the reactor outlet in all cases. Fig. 2a shows that the overall rate of *n*-pentane depletion increased when the *n*-pentane in the feed was increased up to 4 mol%, and then levelled, clearly indicating a saturation of the active sites. In the 1 to 4 mol% *n*-pentane content range, an increase in the hydrocarbon concentration favoured the formation of phthalic anhydride over maleic anhydride and carbon oxides. This suggests that a bimolecular step is involved in the pathway leading to the formation of phthalic anhydride, which is therefore favoured at higher hydrocarbon partial pressures. Above 4% *n*-pentane in the feed, the selectivity to maleic and, mainly, to phthalic anhydride decreased considerably with a corresponding increase in the formation of carbon oxides. This indicates that saturation of the surface sites interferes with the selective pathway to the anhydrides; under these conditions, the adsorbed intermediates are burnt to carbon oxides.

The by-products formed (Fig. 2b) were the same as those mentioned above, plus acrylic acid which is formed above an *n*-pentane concentration of 10 mol%. Also in this case, relationships between the observed by-products and the maleic and phthalic anhydrides could not be extrapolated. However, it is shown that the formation of by-products increased in correspondence with the saturation of the active sites and the fall in the selectivity to the anhydrides, perhaps as a result of the scarce availability of oxidized surface sites.

A number of other by-products could be identified, which although formed in very low amounts, are significant, because they can give useful indications about the multifunctional properties of the catalyst surface. These by-products are reported in Fig. 3, together with the most reasonable pathways for their formation; they can be classified as follows:

(1) Saturated products with 5 carbon atoms: 2- and 3-pentanone, pentan-2,4-dione, 2-methyltetrahydrofuran, γ-valerolactone. The presence of these products indicates the ability of the catalyst to attack the saturated hydrocarbon directly.

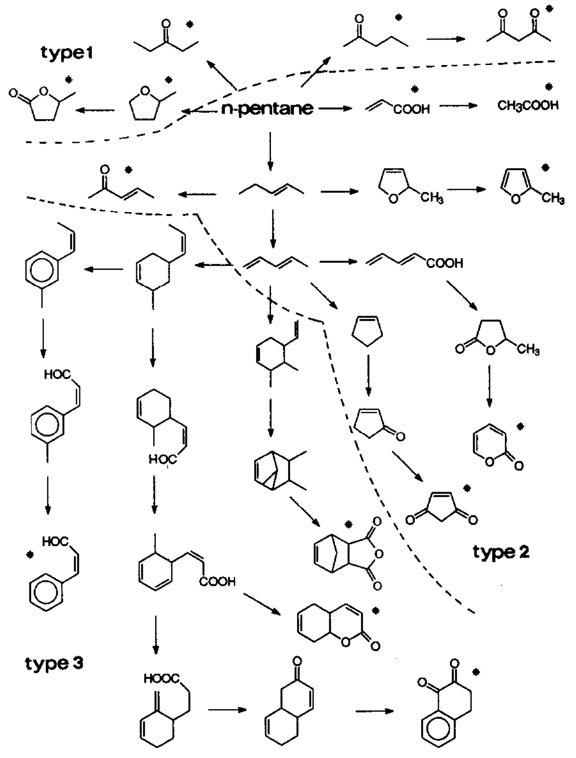


Fig. 3. Possible reaction pathways for the synthesis of by-products obtained in the oxidation of *n*-pentane. See text for explanation. Products with an asterisk were those effectively identified.

(2) Unsaturated products with 5 or less than 5 carbon atoms: acrylic acid, acetic acid, 3-penten-2-one, 2-methylfuran, cyclopent-2-en-1,4-dione, 2H-pyran-2-one. These products are formed through oxidation reactions of pentene, cyclopentene and pentadiene, as well as from oxidative cleavages or cracking reactions.

(3) Unsaturated or aromatic products with more than 5 carbon atoms. The synthesis of these compounds must necessarily take into account the formation of a dimer from an unsaturated C_5 molecule, which after cyclization may be oxidehydrogenated to yield alkylaromatic compounds, and be oxidized to a number of different products.

Obviously, the question remains open whether or not any of these products are intermediates in the formation of the maleic or phthalic anhydrides (desorbing into the gas phase under these conditions), or are only representative of parallel pathways of minor importance. For instance, the 5-norbornene-endo-2,3 dicarboxylic anhydride is a potential precursor for the formation of phthalic anhydride. This compound might form either by the Diels–Alder addition between the maleic anhydride and cyclopentadiene (but in this case we should expect a consecutive reaction with maleic anhydride in favour of phthalic anhydride), or by an intramolecular addition in vinyldimethylcyclohexene (a C_{10} compound formed by dimerization and cyclization of pentadiene) between the double bonds in the ethylidene group and in the cyclohexene ring, with formation of an alkylbicycloheptene, which may finally lose one carbon atom and be oxidized to the 5-norbornene-endo-2,3 dicarboxylic anhydride. However, the absence of any kinetic relationship between the adduct and the phthalic anhydride does not allow a definite conclusion to be drawn.

3.2. *Oxidation of 2-pentene and pentadiene*

The oxidation of 2-pentene was carried out under the same conditions which were employed for the oxidation of *n*-pentane. The trend of the selectivity as a function of residence time is plotted in Fig. 4a and Fig. 4b. The olefin was much more reactive than *n*-pentane, and total conversion was already reached at $W/F = 2$ g s/ml. The main products were carbon oxides, while the selectivity to maleic and phthalic anhydrides was not higher than 10–15%. Other by-products which formed in minor amounts were acetic acid, acrylic acid, pentenone, 2H-pyran-2-one, citraconic acid, cinnamaldehyde and 5-norbornene-endo-2,3-dicarboxylic anhydride. These are the same by-products as those obtained in the oxidation of *n*-pentane, and none of them were found for W/F values higher than 2 g s/ml.

The similar nature of the products obtained from pentane and pentene suggests that the latter (or, better, an adsorbed olefinic-like compound) may be an intermediate product in the oxidation of *n*-pentane. The lower selectivity to maleic and phthalic anhydrides from the olefin can be due to the high amount of side products of partial oxidation, which are precursors for the formation of carbon oxides. On the contrary, when starting from the paraffin, the intermediate adsorbed olefinic compound is quickly transformed to the final anhydrides. Another possible explanation for the difference in selectivity observed may be attributed to the higher degree of interaction between the olefin and the

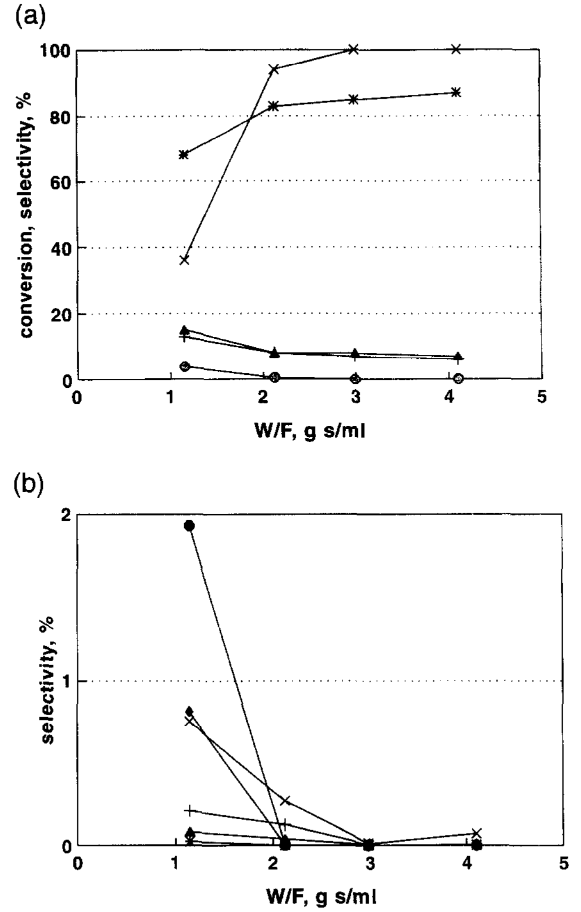


Fig. 4. (a) 2-Pentene conversion (×), and selectivity to maleic anhydride (△), phthalic anhydride (+), carbon oxides (∗) and other by-products (O) as functions of the W/F ratio. (b) Selectivity to 2H-pyran-2-one (O), citraconic anhydride (×), 2-penten-2-one (∗), cinnamaldehyde (△), acrylic acid (+) and 5-norbornene-endo-2,3-dicarboxylic anhydride (◇) as functions of the W/F ratio. Conditions: T, 613 K; feedstock, 1 mol% 2-pentene in air; catalyst amount, 3 g.

catalyst surface, which even at low olefin concentration in the gas phase leads to a situation on the catalyst surface similar to the one observed at high *n*-pentane concentration. In fact, the product distribution is exactly the same at 1% 2-pentene and above 10% *n*-pentane in the feed (compare Fig. 4a and Fig. 2a). This also agrees with that reported by other authors [5], who found that 2-pentene interacts with the catalyst surface much more strongly than *n*-pentane.

The oxidation of pentadiene yielded the same products as from 2-pentene. The diolefin was more reactive than the olefin, and total conversion of the diolefin was obtained already at $W/F = 1$ g s/ml. Also in this case, the selectivity to maleic and phthalic anhydrides was not higher than 10–15%. These data suggest that the adsorbed pentene may be quickly transformed to the diolefin, which constitutes the second intermediate species in the multistep oxidation of *n*-pentane. The several by-products obtained indicate that pentadiene may either be oxidized up to maleic anhydride or, alternatively, dimerize and be converted to an alkylaromatic compound, precursor of phthalic anhydride formation.

3.3. Surface acidity of vanadyl pyrophosphate

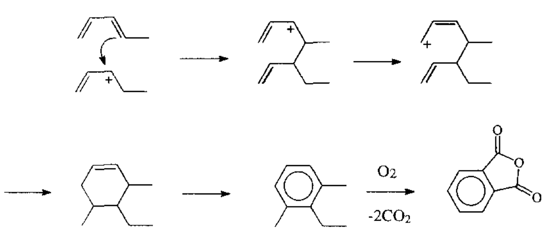
The by-products identified in the oxidation of *n*-pentane, 2-pentene and pentadiene point out the possible role played by the surface acidity of vanadyl pyrophosphate. In order to verify the effective activity of the catalyst in an acid-catalyzed reaction, the catalytic performance of vanadyl pyrophosphate in the alkylation of benzene with propylene was checked, and compared with that of an industrial catalyst for the synthesis of cumene, which consists of polyphosphoric acid supported over silica. This comparison is homogeneous, since the surface acidity of $(VO)_2P_2O_7$ may originate from the presence of pendant P–OH groups, besides the Lewis acidity of V^{4+} species. The conversion of benzene and the selectivity to cumene for the two catalysts examined are compared in Table 1. It is shown that vanadyl pyrophosphate, though being less active than phosphoric acid in the alkylation of benzene, nevertheless is characterized by a non-negligible activity. This surface acidity may also be responsible for the pentene or pentadiene transformation to C_{10} aromatic compounds.

Table 1
Catalytic performance of vanadyl pyrophosphate and supported phosphoric acid in the alkylation of benzene with propylene to cumene in batch reactor

Catalyst	Time of reaction (h)	Cumene yield (%)	Cumene selectivity (%)
VPO	1	1.5	83
	3	2.5	86
	5	2.7	84
H_3PO_4/SiO_2	1	12.5	87
	3	17	89
	5	18	90

In order to confirm this hypothesis, 1% pentadiene diluted in nitrogen was fed into the reactor, at 613 K. Several products containing 10 carbon atoms formed with very low yields, among which the most relevant were different alkylbenzenes, such as ethyl-dimethyl, methyl-isopropyl, methyl-propyl, diethyl and tetramethylbenzene. It is worth mentioning that these alkylaromatics were not found when the reaction was carried out in the presence of molecular oxygen. In addition, minor amounts of 1-methyl-1H-indene, and of products containing less than 10 carbon atoms, such as 1,3,5-cycloheptatriene, furan, and other alkylaromatics, also formed.

When 2-pentene was fed under the same conditions, thus in the absence of molecular oxygen, no formation of alkylaromatics was detected. On the contrary, the same products were obtained with a cyclopentene feed. The anaerobic transformation of butadiene led to the formation of styrene and ethylbenzene as the prevailing products, with yields however lower than 1%. Minor amounts of other products were



Scheme 1.

also identified: 1,3,6-octatriene, ethylidencyclohexene, 2,5-dihydrofuran, toluene and benzene.

These data indicate that the acid properties of the catalyst are able to catalyze the transformation of the diolefin to the alkylaromatic, possibly through the mechanism shown in Scheme 1: the pentadiene dimerizes to a branched C_{10} olefin, which may easily yield a cyclic unsaturated compound (i.e. alkylcyclohexenes); the latter may finally yield the alkylaromatic via an H-transfer mechanism.

It is worth noting that whereas the pentadiene yielded a number of different alkylaromatics, butadiene almost exclusively yielded ethylbenzene and styrene. This would seem to indicate that either a concerted conjugation of two butadiene molecules (such as an uncatalyzed Diels–Alder condensation, kinetically favoured at the adsorbed state), or a nucleophilic addition of one butadiene molecule to a second butadiene coordinated to a Lewis acid center, may be the true mechanism, rather than a less specific proton-catalyzed reaction (which should necessarily also lead to the formation of dimethylcyclohexene, the *o*-xylene precursor, rather than ethylcyclohexene, precursor of ethylbenzene).

Whichever the mechanism for the pentadiene transformation to the unsaturated C_{10} compound may be, this reaction is clearly thermodynamically unfavoured at high temperatures, even though the equilibrium may likely be displaced by the consecutive reactions occurring in the oxidizing environment, such as the aromatization by oxidehydrogenation, the partial oxidation of the alkylaromatic to phthalic anhydride (with loss also of two carbon atoms) or the total oxidation to carbon oxides. This might also explain the maximum observed for the yield to phthalic anhydride when the reaction temperature is increased above 593 K. It is worth mentioning that the yield to maleic anhydride does not exhibit this maximum, but rather continuously increases up to total *n*-pentane conversion [3].

Finally, the formation of only ethylbenzene (and not of *o*-xylene) in the anaerobic transformation of butadiene explains the very low selectivity to phthalic anhydride obtained in the oxidation of *n*-butane.

3.4. Reactivity of o-xylene

Finally, tests were done with a 1% *o*-xylene feed in air at 613 K, in order to verify the ability of the catalyst to oxidize the alkylaromatic to phthalic anhydride, and to find support for the mechanism proposed. Fig. 5 compares the hydrocarbon conversion and the productivity to phthalic anhydride for the oxidation of *n*-pentane and of *o*-xylene. It is shown that *o*-xylene is more reactive than the paraffin. This might explain the absence of C_{8+} alkylaromatic by-products in the oxidation of *n*-pentane (but indeed some corresponding products of oxidation were detected, as shown in Fig. 3). If we

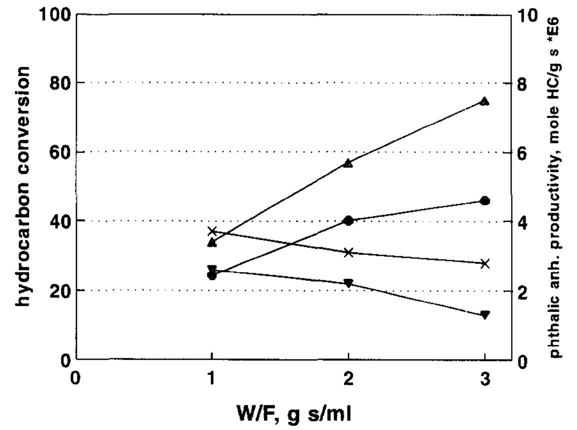
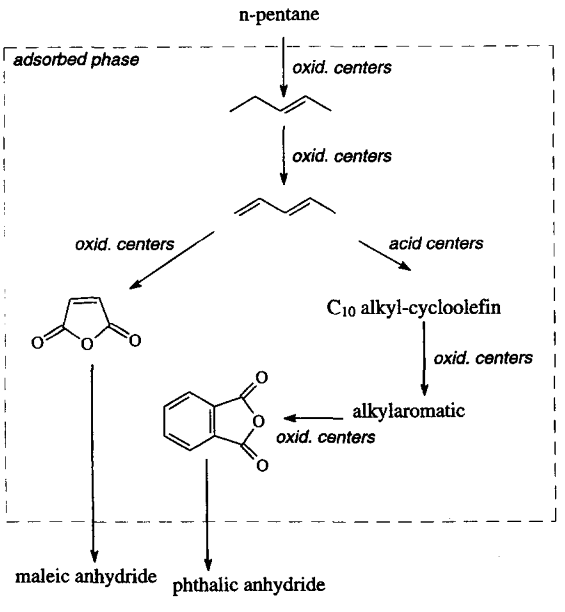


Fig. 5. *o*-Xylene conversion (△), *n*-pentane conversion (○), productivity of phthalic anhydride from *o*-xylene (×) and productivity of phthalic anhydride from *n*-pentane (▽) as functions of the *W*/*F* ratio. Conditions: *T*, 613 K; feedstock, 1 mol% hydrocarbon in air; catalyst amount, 3 g.

make the reasonable hypothesis that the activation and oxidehydrogenation of *n*-pentane to pentene is the rate-determining step, this means that as soon as the alkylaromatic (or any other intermediate adsorbed product) is formed it is quickly transformed to phthalic anhydride before it can desorb. This explains the formation of only maleic anhydride, phthalic anhydride and carbon oxides under usual reaction conditions.

4. Conclusions

The mechanism proposed for the oxidation of *n*-pentane over vanadyl pyrophosphate on the basis of the results obtained is shown in Scheme 2: the paraffin is activated and first oxidehydrogenated to pentene and then to pentadiene. The diolefin can follow two different pathways. The first involves formation of a cyclic C_{10} unsaturated compound (likely by acid-catalyzed dimerization followed by intramolecular cyclization), which then can be converted to alkylaromatics via an H-transfer mechanism (or more likely, in the presence of molecular oxygen, via an irreversible oxidehydrogenation). Dimerization reactions are unfavoured at high temperature, but are displaced in favour of the products by the consecutive, irreversible oxidation of two neighbouring alkyl groups in the alkylaromatic (which also loses two carbon atoms), with formation of the diacid and then of the very stable phthalic anhydride, which finally desorbs into the gas phase. The second, involves oxidation of pentadiene to maleic anhydride via a multi-step route, analogous to that proposed for the formation of maleic anhydride from *n*-butane.



Scheme 2.

Acknowledgements

This work was supported by MURST. Dr. Alessandra Primavera, from University of Udine, is gratefully acknowledged for performing the GC-MS analysis.

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