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ON THE POLYFUNCTIONAL NATURE OF $(VO)_2P_2O_7$

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Vanadyl pyrophosphate catalyst, selective oxidation of alkanes and aromatics

The catalytic behavior of vanadyl pyrophosphate in the conversion of decalin, tetrahydro phthalic anhydride, naphthalene, 3-methyl tetrahydrophthalic anhydride, and benzene is reported in order to evidence some basic key catalytic properties of this catalyst and to discuss the possible surface pathways in the synthesis of phthalic anhydride from n-pentane, a characteristic specific catalytic property of this system.

1. Introduction

$(VO)_2P_2O_7$ is a well known catalyst for the selective oxidation of n-butane to maleic anhydride [1]. The reaction mechanism involves a series of H-abstraction and O-insertion steps [2] and may be outlined as follows:

n-butane → butenes → butadiene → tetrahydrofuran → furan → maleic anhydride.

Recently, the formation of relevant amounts of phthalic anhydride from n-pentane on vanadyl pyrophosphate has been shown [3]. The reaction mechanism in this synthesis is probably relatively similar to that for the synthesis of maleic anhydride from n-butane, but involves the additional step of C–C bond formation. The absence of detectable intermediates in the usual conditions of reaction (around 1–2% hydrocarbon and 20% O_2 at atmospheric pressure) prevents any more detailed conclusion. However, it has been shown [4] that gas phase Diels Alder reactions do not take place and that the phthalic anhydride formation is parallel to maleic anhydride formation. The reaction of C–C bond formation occurs probably through surface-enhanced pseudo-Diels Alder, template or radical dimerization reactions between adsorbed intermediates.

Based on these hypotheses, two main reaction patterns can be suggested as model pathways (scheme 1), involving the consecutive transformation of decalin or of methyl-tetrahydrophthalic anhydride. The first pathway can be assumed as

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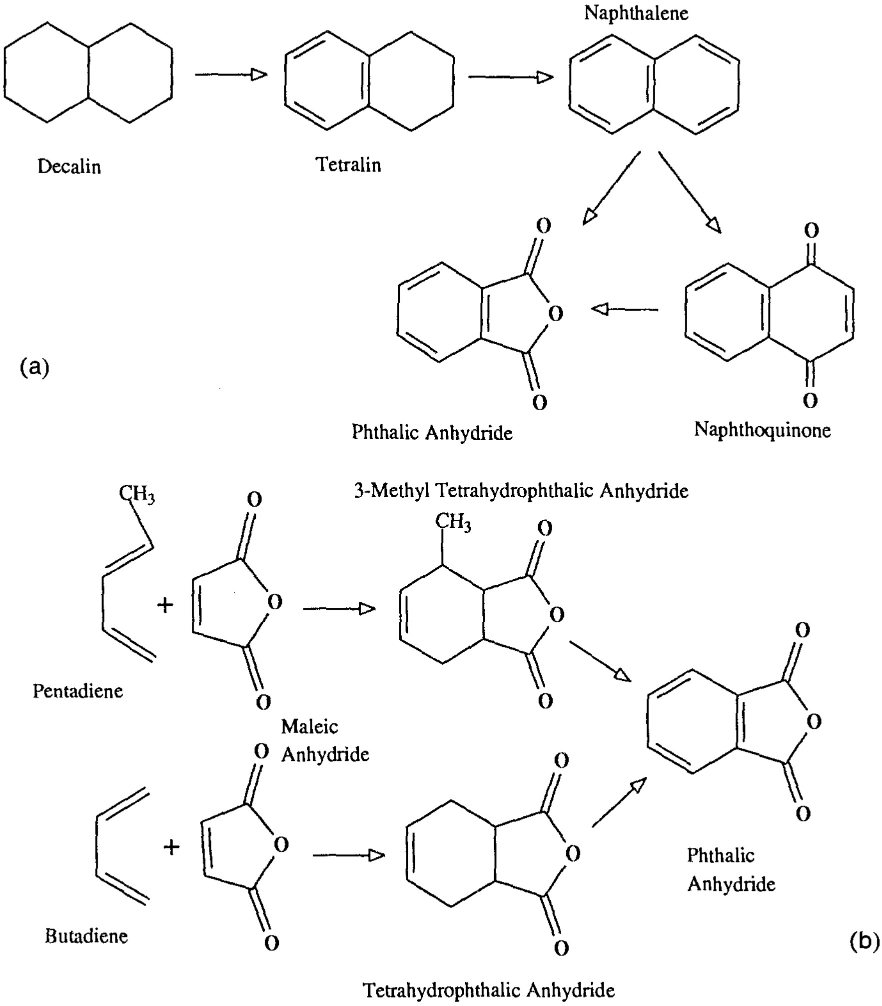


Scheme 1. (a, b). Model reaction patterns after the step of C–C bond formation in the synthesis of phthalic anhydride from n-pentane on $(VO)_2P_2O_7$.

a model for the consecutive transformation of an intermediate derived from the pseudo-Diels Alder or template reaction between two adsorbed hydrocarbons (such as the possible intermediates C_5 olefins or cyclopentadiene [4]). The second pathway can be taken as a model for the reaction between pentadiene and an O-containing adsorbed product or intermediate such as maleic anhydride.

The analysis of the reactivity of C_5 olefins [4] does not provide useful data about these aspects due to their strong self-inhibition effect on the selectivity. In this paper we report therefore the reactivity of some of these possible intermediates (see scheme 1) in order to (i) gain information about the mechanism of phthalic anhydride formation from n-pentane and (ii) explore the catalytic behavior of vanadyl pyrophosphate towards new types of reactions. The reagents were chosen to evidence the presence of specific properties of the catalyst such as (i) H-abstraction from paraffinic C–H bonds, (ii) aromatization of saturated or unsaturated rings, (iii) 1–4 oxygen insertion and (iv) formation of C–C bonds possibly through template reactions that may be useful to clarify some aspects of the mechanism of synthesis of phthalic anhydride from n-pentane.

2. Experimental

2.1. PREPARATION OF $(VO)_2P_2O_7$

V_2O_5 (50 g) was stirred into 0.6 L of a technical-grade mixture (1 : 2) of benzyl and isobutyl alcohols. Orthophosphoric acid (in such an amount as to give a final P : V ratio of 1.1) dissolved in 0.1 L of isobutyl alcohol was then added to form a slurry which gradually darkened upon heating to the reflux temperature (approximately 110 ° C). After several hours, the mixture was cooled with continued stirring. The light-green product was isolated by filtration, washed, and then dried overnight at 150 ° C. Both X-ray diffraction patterns and infrared examination indicated the solid to be $[VOHPO_4]_2 \cdot H_2O$. The vanadyl hydrogen phosphate hemihydrate was then calcined at 400 ° C in a mixture of 1.5% butane/air until steady-state conversion of butane to maleic anhydride was well established. The reactor was then cooled; the solid recovered was shown to be pure $(VO)_2P_2O_7$ by chemical, infrared and X-ray diffraction analyses.

All the catalytic tests were made on a $(VO)_2P_2O_7$ catalyst which had been treated in a flow of butane/air at about 380 ° C for more than 700 hours in order to reach steady-state behavior in the conversion of n-butane to maleic anhydride. The treatment was thought to be necessary in order to analyze the surface catalytic properties of a representative sample in the n-butane oxidative conversion [5].

2.2. FLOW REACTOR CATALYTIC TESTS

Catalytic tests under steady-state conditions were made in a continuous down-flow fixed-bed integral apparatus [3]. The flow reactor was charged with 4 g of sample with particle dimensions in the range 0.125–0.250 mm. The reactor was provided with an axial thermocouple sliding inside in order to control isothermicity (within 3–4 ° C) during catalytic runs. The absence of significant diffusional limitations (heat and mass transfer) to the rate of hydrocarbon depletion was verified experimentally by varying the feed rate at a constant catalyst weight/reagent flow rate (W/F) ratio, and testing catalysts with different particle sizes. Additional calculations (thermal balance over the catalyst granules using the Colburn analogy, determination of the Biot number) indicated the isothermicity of the whole particle.

The reactor assembly was interfaced between the section of the reagent mixture preparation and flow control and the section for reagent mixture analyses of the reagent composition and of the reaction products. The outlet stream from the reactor was kept at 220 ° C to prevent condensation of organic products that were analyzed in a first gas chromatograph using a flame ionization detector. After cooling the gas stream, oxygen, nitrogen, carbon monoxide and carbon dioxide were analyzed in a second gas chromatograph using a thermal conductivity detector. A 3-m Porapak QS column was utilized in the first chromatograph, and the oven temperature was programmed to rise from 70° to 220° C at 16° C min^{-1}. The second chromatograph was operated with a Carbosieve-II column, and the oven temperature was programmed to increase from room temperature to 225 ° C at 16 ° C min^{-1} after an initial 9 min under isothermal conditions.

3. Results

The conversion of decalin and the selectivities in the formation of tetralin (TET), naphthalene (NAP), naphtoquinone (NQ) and phthalic anhydride (PA) are shown in fig. 1a. High selectivities to the products of oxidative dehydrogenation with aromatization are detected at low reaction temperatures (below 310 ° C), whereas at higher temperatures products of oxygen insertion (NQ and PA) are also observed. The formation of these last two products derives from the consecutive transformation of the intermediate naphthalene as shown by its selective conversion to PA and NQ (fig. 1b). The vanadyl pyrophosphate is slightly less active in the conversion of naphthalene in comparison with decalin indicating that the catalyst is more active in H-abstraction from an alkane molecule than in oxidative attack (with oxygen insertion) of the aromatic ring.

The conversion of tetrahydrophthalic anhydride and the selectivities to phthalic anhydride (PA) and benzene (Ph) are shown in fig. 2a. The reaction is very selective to PA at relatively low temperatures indicating the high activity of vanadyl pyrophosphate in the selective dehydrogenation to form an aromatic ring. At higher temperatures, the selectivity decreases due to the formation of benzene and carbon oxides. In the case of 3-methyl tetrahydrophthalic anhydride (fig. 2b) the main product observed at low temperatures is 3-methylphthalic anhydride (3MePA). At higher temperatures the selectivity decreases due to demethylation with formation of phthalic anhydride and at even higher temperatures due to the formation of benzene and carbon oxides. These data indicate the instability during oxidation on vanadyl pyrophosphate of a lateral methyl group to an activated aromatic ring. It is likely that the lateral methyl group is oxidized to a carboxylic acid group with consecutive easy decarboxylation.

The activity of vanadyl pyrophosphate in the conversion of benzene is reported in fig. 3. Benzene is a useful test molecule to verify the possible occurrence of template reactions on the surface leading to the formation of C–C bonds.

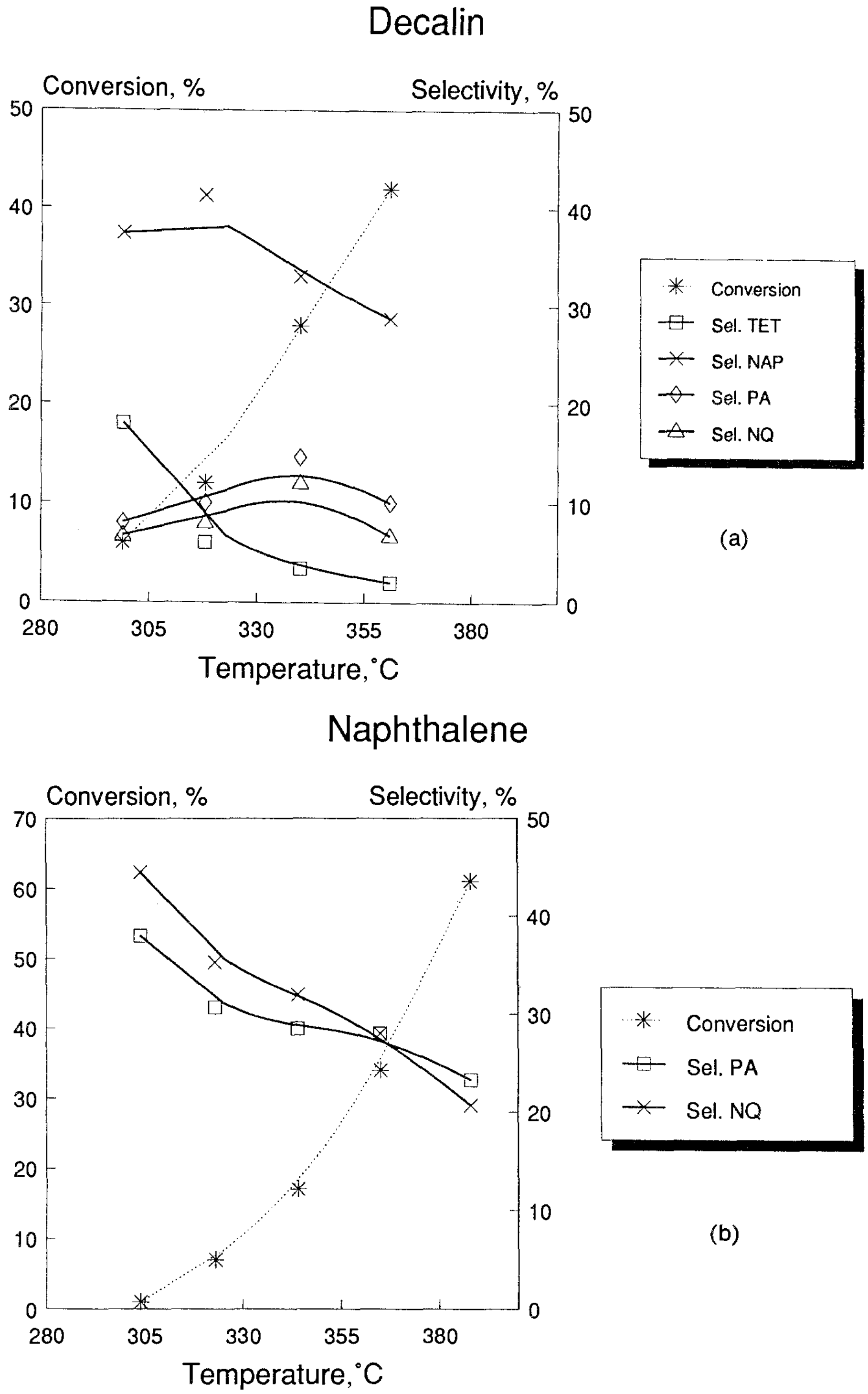
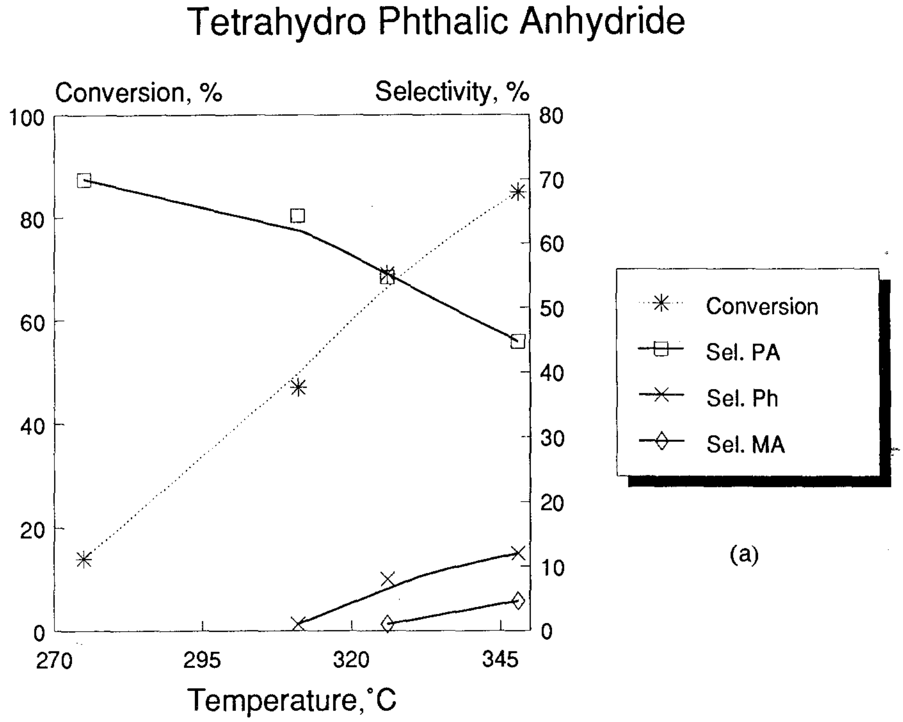


Fig. 1. Catalytic behavior of $(VO)_2P_2O_7$ in the selective conversion of decalin (a) and of napthalene (b). Experimental conditions: 2 g of catalyst, (a) 2.2% decalin, 15.6% O_2, $W/F = 314$ g.h $(\text{moles}_{\text{reagent}})^{-1}$. (b) 1% napthalene, 14% O_2, $W/F = 705$ g.h. $(\text{moles}_{\text{reagent}})^{-1}$.



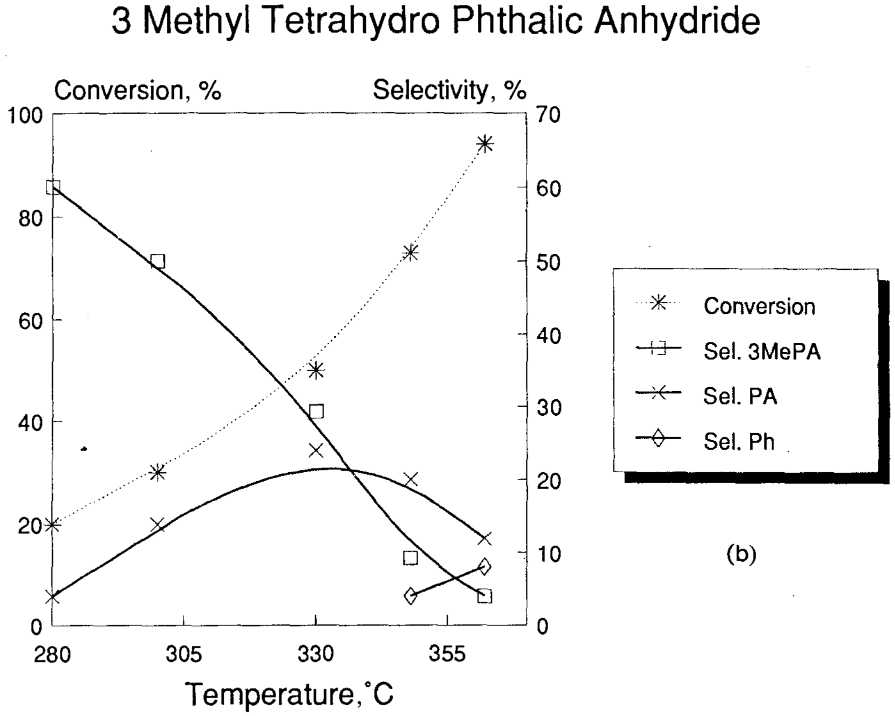


Fig. 2. Catalytic behavior of $(VO)_2P_2O_7$ in the selective conversion of tetrahydrophthalic anhydride (a) and of 3-methyl tetrahydrophthalic anhydride (b). Experimental conditions: 2 g of catalyst, (a) 0.4% tetrahydrophthalic anhydride, 19% O_2, $W/F = 1300$ g.h $(\text{moles}_{\text{reagent}})^{-1}$. (b) 1% 3-methyl tetrahydrophthalic anhydride, 10% O_2, $W/F = 415$ g.h $(\text{moles}_{\text{reagent}})^{-1}$.

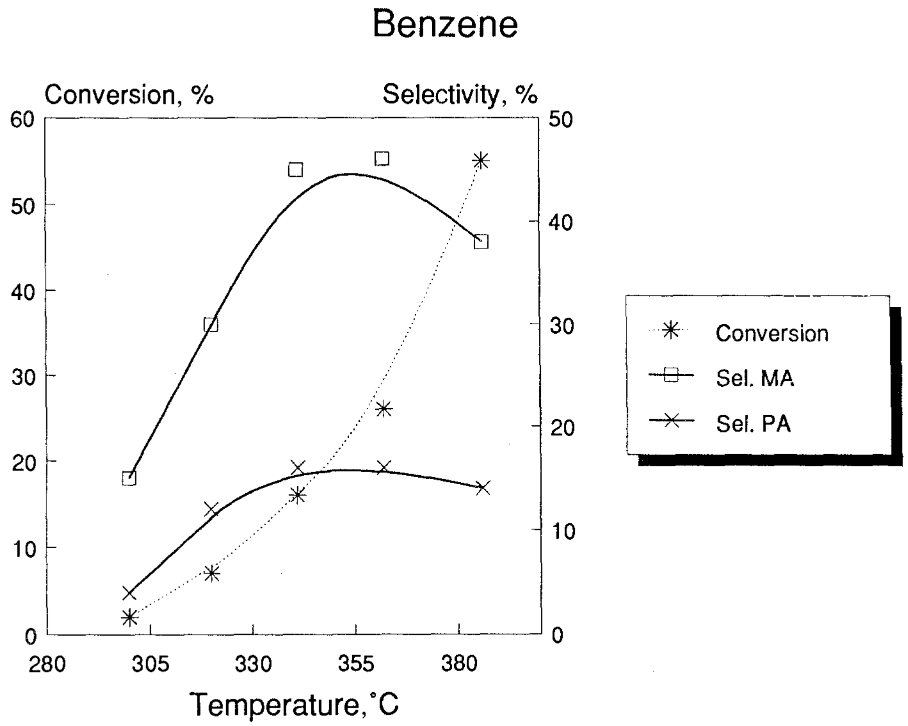


Fig. 3. Catalytic behavior of $(VO)_2P_2O_7$ in the selective conversion of benzene. Symbols: see scheme 1. Experimental conditions: 2 g of catalyst, 2% benzene, 13% O_2, $W/F = 328$ g.h $(\text{moles}_{\text{reagent}})^{-1}$.

Together with the relevant formation of maleic anhydride (MA), phthalic anhydride (PA) is also detected in significantly high amounts. This suggests by analogy that the surface template reaction between two adsorbed cyclopentadiene molecules may be the key step in the formation of phthalic anhydride from n-pentane.

4. Discussion

These results clearly illustrate the following three specific properties of vanadyl pyrophosphate:

1) Oxidative dehydrogenation

Very high selectivities in products of oxidative dehydrogenation were observed at low conversion for decalin to tetralin and in the conversion of 3-methyltetrahydro- and tetrahydro-phthalic anhydride. These reactions can be taken as test reactions to reveal oxidative dehydrogenation properties. In the case of n-butane and n-pentane oxidation the formation of the corresponding olefins and diolefins was hypothesized, but not directly shown due to the simultaneous occurrence of the reaction of oxygen insertion.

2) 1–4 Oxygen insertion

The formation of naphthoquinone can be taken as a test reaction to reveal the presence of a reaction of 1–4 oxygen insertion in a diene group. This reaction is the analogous to that for the formation of tetrahydrofuran in the 1–4 oxygen insertion in butadiene. The oxidation of benzene to maleic anhydride also can be considered a 1–4 oxygen addition but cannot be taken as diagnostic for this type of oxygen insertion.

3) Increased carbon chain length

The formation of phthalic anhydride from benzene as well as that from n-pentane is evidence that this is also a specific functionality of vanadyl pyrophosphate.

Taking into consideration that (i) only traces of phthalic anhydride are detected in the oxidation of n-butane, (ii) the reasonably similar pathways in the oxidation of n-butane and n-pentane but the additional possible formation of a cyclic intermediate (cyclopentadiene) from the C_5 alkane and (iii) the relatively high selectivity to phthalic anhydride from benzene, a template surface reaction between two adsorbed cyclopentadiene molecules may be tentatively assumed as the key step in the synthesis of phthalic anhydride from n-pentane.

The comparison of the reactivity of the two possible model reaction patterns (scheme 1) indicates that after the step of C–C bond formation between two adsorbed hydrocarbons (first model pathway–scheme 1a) or between an adsorbed hydrocarbon and an O-containing molecule (second model pathway–scheme 1b) both reactions proceed selectively to phthalic anhydride. A lateral methyl group is oxidized with decarboxylation in a range of temperatures comparable to that of oxygen insertion on an aromatic molecule and therefore the absence of detection of the methylphthalic anhydride in the outlet stream during n-pentane oxidation is not indicative of the reaction pattern.

These data thus indicate that both mechanisms are possible, even though the behavior of the vanadyl pyrophosphate in the oxidation of benzene is suggestive of a reaction pattern involving the surface reaction between two adsorbed cyclopentadiene intermediates.

4. Conclusions

The use of different probe molecules may be successfully applied for the evaluation of surface catalytic properties of vanadyl pyrophosphate in order to distinguish between H-abstraction properties and O-insertion properties and to evaluate other basic key catalytic properties. The information obtained clarifies some aspects of the complex reaction mechanism of n-butane and n-pentane conversions on this catalyst, which are the most characteristic reactions of vanadyl pyrophosphate with important industrial applications [1]. The development of suitable test reactions able to single-out some key features of the surface reactivity of the catalyst provides the basis for a rational comparison with other catalytic systems in order to clarify the unique catalytic properties of this system in the selective conversion of linear C_4 and C_5 alkanes to anhydrides.

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References

[1] G. Centi, F. Trifiro', J.R. Ebner and V.M. Franchetti, Chem. Rev. 88 (1988) 55.
[2] G. Busca and G. Centi, J. Am. Chem. Soc. 111 (1989) 46.
[3] G. Centi, J. Lopez Nieto, D. Pinelli, F. Trifiro', Ind. Eng. Chem. Research 28 (1989) 400.
[4] G. Centi, J. Lopez Nieto, D. Pinelli, F. Ungarelli and F. Trifiro', In: *New Developments in Selective Oxidation*, eds. G. Centi and F. Trifiro' (Elsevier Science Pub., Amsterdam, 1990) in press.