A novel route in partial oxidation of *n*-pentane over the VPO catalysts: formation of citraconic anhydride

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Oxidation of *n*-pentane on bismuth-doped vanadyl pyrophosphate was shown to give three anhydrides: maleic, phthalic and citraconic. The presence of a bismuth additive ($Bi/V = 0.1$) increases the selectivity to citraconic anhydride which is formed via skeletal isomerization of *n*-pentane to isopentane, followed by its oxidation. Phthalic anhydride seems to be formed via condensation of maleic anhydride with intermediate C_4 olefins.

Keywords: citraconic anhydride; oxidation of *n*-pentane; VPO catalysts

1. Introduction

It is now generally accepted [1,2] that one of the parameters, responsible for the specific activation of $(VO)_2P_2O_7$ catalysts in the partial oxidation of *n*-butane to maleic anhydride, is connected with the geometric correspondence between the structural unit of the catalyst playing the role of the active site and the molecule to be oxidized. The appropriate separation between these units enables also the site isolation principle to operate. It is assumed that in the case of the oxidation of *n*-butane, the activation of C–H bonds in both terminal methyl groups, i.e. at the first (C1) and fourth (C4) carbon atoms, takes place as the first step of the oxidation. Theoretical calculations [3,4] confirmed a high probability of this mechanism.

According to this hypothesis, it can be expected that activation of *n*-pentane on $(VO)_2P_2O_7$ should also occur at C1 and C4 atoms. As a result, the $(C5)H_3$ group should be split off and maleic anhydride formed. Experimental data described in refs. [5,6] have confirmed this supposition.

On the other hand, the presence of strong acidic centres on the surface of VPO catalysts [1,7] could lead to the skeletal isomerization of *n*-pentane and in the case of *n*-pentane oxidation, methylmaleic (citraconic) anhydride could be obtained. However, this compound has never been observed as a product of *n*-pentane oxidation but considerable amounts of phthalic anhydride were detected [5,6,8,9] instead. Thus the mechanism of *n*-pentane transformation remains to be clarified.

It seemed therefore of interest to undertake a study with the aim to verify the possibility of the citraconic anhydride formation over VPO catalysts, and to try to describe the mechanism of *n*-pentane transformation.

2. Experimental

The VPO catalysts were prepared from V_2O_5 and H_3PO_4 in butanol medium [10]. The composition of the investigated catalysts is given in table 1.

The phase composition of the samples was determined with a DRON-3.0 diffractometer using Cu Kα radiation. The acidic properties of the surface were investigated with the TPD method [10]. The surface morphology and composition were studied by scanning electron microscopy (Jeol JSM-35 SF and Ortek EEDS-II) and XPS (VG ESCA-3) [10].

Catalytic oxidation of *n*-pentane was carried out in a fixed-bed flow reactor using reaction mixtures of two compositions: 1.9 and 3.7 vol% n-C_5H_{12} in air. Gas-chromatography was used for product analysis. For identification of the products also mass-spectrometry was used, the experimental procedure (condensation in ethanol) being described in ref. [11].

To obtain the catalysts with a stationary state of the surface (conditioned catalysts), the VPO and VPBiO catalysts were exposed to the oxidation reaction of *n*-butane (1.8 vol% in air) during 80 h at the temperature of 440°C.

3. Results

The XRD data show that before catalytic tests all samples under investigation contain the $VOHPO_4 \cdot 0.5H_2O$ phase with the most intensive lines at $d = 0.570$, 0.453, 0.367, 0.311, 0.294, 0.279 and 0.266 nm. An excess of phosphorus in the samples practically does not cause any change in the pattern intensities. Some additional lines at $d = 0.442$, 0.352, 0.303, 0.286, 0.237 and

0.216 nm are observed for the samples containing bismuth. These peaks are attributed to the bismuth phosphate phase, in good agreement with the literature data [12].

The analysis of the phase composition of the conditioned catalysts (*n*-butane oxidation for 80 h) shows the presence of the vanadyl pyrophosphate [$(VO)_2P_2O_7$] phase only with the most intensive reflections at 0.387, 0.314, 0.298, 0.244, 0.209 nm. In XRD patterns of the samples with bismuth, besides the main phase of $(VO)_2P_2O_7$, bismuth phosphate lines (see above) were also observed.

At the VPBiO-2 catalyst surface, as revealed by scanning electron microscopy, beside the basic vanadyl pyrophosphate phase, also another, different phase (phase F) was present. It is more clearly seen in the BEI regime exposure (fig. 1a). The study of the characteristic V Kα radiation from this part of the surface (fig. 1b) shows the minimum of the vanadium density at the phase F. On the other hand at this place the maximum density of bismuth was found by Bi Lα-radiation (fig. 1c). Simultaneously, phosphorus is uniformly distributed over all surfaces investigated.

Results of the XPS study of the samples are given in table 1. It can be noted that the binding energy of V 2p and P 2p electrons is practically unaffected by the sample composition. The binding energy (BE) of O 1s electrons slightly increased with the higher phosphorus content in the catalyst. BE of Bi 4f electrons was measured significantly higher ($\Delta E = 0.9$–1.1 eV) as compared to the literature data for bismuth phosphate [13].

It may be noted from the relative content of elements as determined by XPS (table 1) that phosphorus is in excess on the surface as compared to its content in the catalyst bulk. Moreover, the surface concentration of phosphorus increases with the introduction of bismuth additive. Also the surface concentration of bismuth exceeds that in the bulk.

The ammonia thermodesorption study (table 1) shows, that the relative surface content of phosphorus is in good correlation with the total amount (A) of adsorbed ammonia, which corresponds with the number of acidic centres. Simultaneously, changes of the ratio of the number (C) of strong acidic centres (desorption at $T > 300°C$) and their total number (A) follow the same trend.

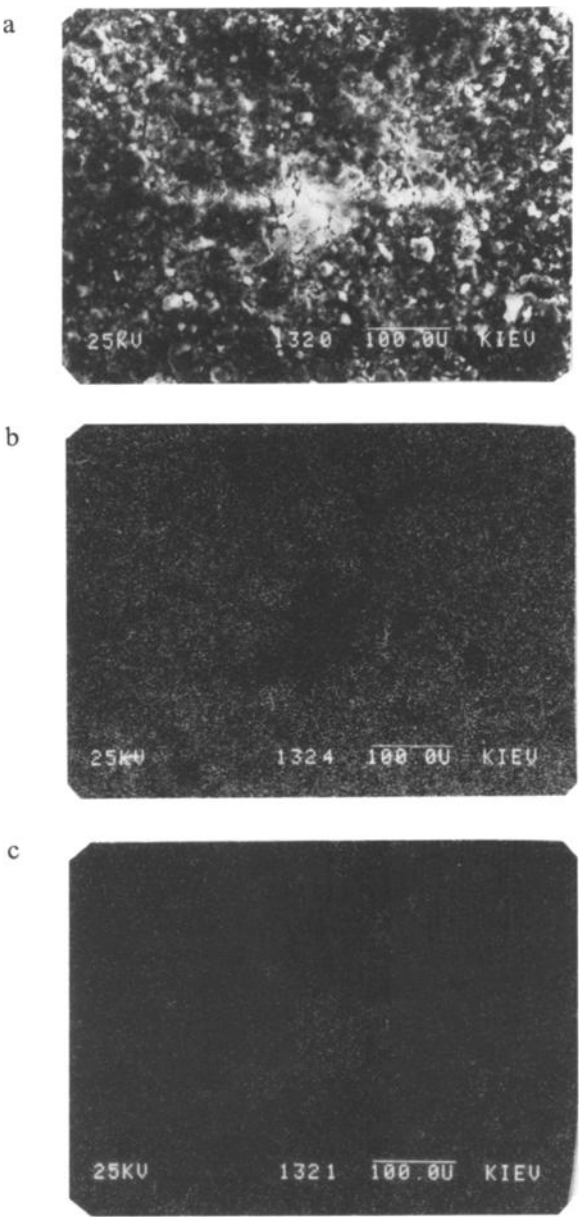


Fig. 1. SEM investigations of VPBiO-2 catalyst surface: (a) BEI regime, (b) V Kα radiation, (c) Bi Lα radiation.

Mass-spectra of products of *n*-pentane oxidation over the VPO-1 and VPO-2 catalysts are presented in fig. 2. In all cases the main products observed are phthalic anhydride (PA, 148 mass units), and maleic anhydride (MA,

Table 1
Properties of the catalysts surface

Catalyst	Bulk ratio		Binding energy (eV)				Surface ratio		TPD (NH_3)[a]	
	P/V	Bi/V	O 1s	P 2p	V 2p	Bi 4f	$(P/V)_s$	$(Bi/V)_s$	A	C/A
VPO-1	1.0	–	532.2	133.9	517.7	–	1.23	–	0.12	0.48
VPO-2	1.2	–	532.4	134.1	517.6	–	1.54	–	0.14	0.60
VPBiO-1	1.0	0.1	531.9	134.0	517.5	160.2	1.60	0.18	0.22	0.70
VPBiO-2	1.2	0.1	532.1	134.0	517.5	160.4	1.82	0.16	0.28	0.74

[a] A – total adsorption, cm^3/m^2; C – desorption at $T > 300°C$.

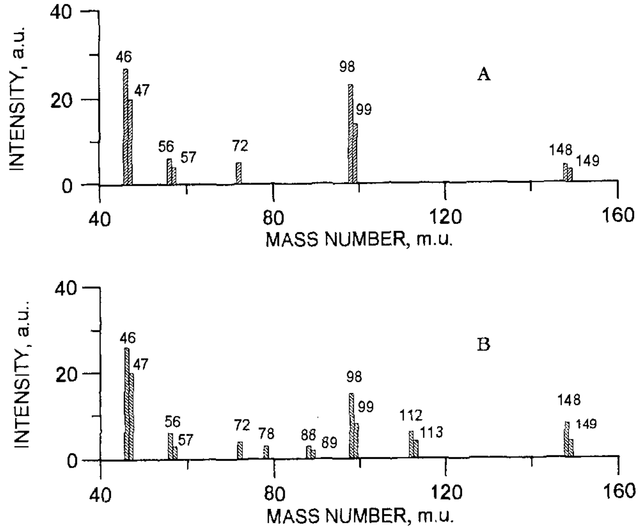


Fig. 2. Mass-spectra of the *n*-pentane (3.7%) oxidation products on (A) VPO-1 and (B) VPO-2. The identification of mass units: 46 – ethanol (solvent), 47 – ethanol proton form, 56 – acrolein or butene, 57 – acrolein proton form, 72 – pentane or acrylic acid or butyraldehyde, 78 – benzene (?), 88 – butyric acid, 89 – butyric acid proton form, 98 – maleic anhydride, 99 – maleic anhydride proton form, 112 – citraconic anhydride, 113 – citraconic anhydride proton form, 148 – phthalic anhydride, 149 – phthalic anhydride proton form.

98 mass units), but on the VPO-2 catalysts citraconic anhydride (MMA, 112 mass units) was also formed. These results of mass-spectroscopic analysis of *n*-pentane oxidation products agree well with those obtained by gas-chromatography.

Fig. 3 shows the dependence of the concentration of products formed in the partial oxidation of *n*-pentane on the reaction temperature. As can be seen, for both reaction mixtures (1.9 and 3.7% of pentane) this temperature dependence for the formation of PA and C_4 olefins passes through a maximum within the 330–350°C temperature region. In the case of maleic and citraconic anhydrides, their concentrations continuously increase with the rise of reaction temperature. This difference between the MA and PA concentration/temperature plots results from a higher oxidation rate of PA as compared to MA [14]. As we found on VPO-2 catalyst (280–340°C), the relative content of PA and MA in the products changes and the PA content increases when the *n*-pentane concentration in the reaction mixture grows. For *n*-pentane content of 1.9 and 3.7 vol% the MA/PA ratio is 1.7–1.9 and 1.3–1.4, respectively. Simultaneously, the MA/MMA ratio practically does not depend on *n*-pentane concentration and amounts to 4.8–5.0.

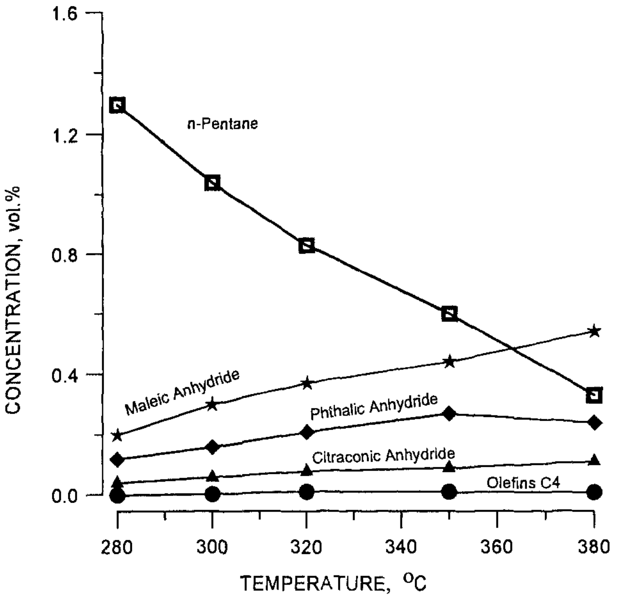


Fig. 3. The temperature dependence of the gas composition in pentane oxidation on the VPO-2 catalyst. Pentane content 1.9%, SV = 2000 h^{-1}.

Conversion of *n*-pentane and selectivities to the main products in the oxidation of *n*-pentane on all the studied catalysts are presented in table 2.

Important changes in the product composition resulted from a variation in phosphorus and bismuth content. After the 0.2 excess of phosphorus was introduced to VPO-1, MMA appeared in the products, the selectivity towards PA somewhat decreased while the selectivity to MA remained practically unchanged. An introduction of bismuth into the VPO-1 catalyst also leads to MMA formation, the selectivity to PA decreases but to MA increases.

When the paraffin concentration in the reaction mixture increases some decrease of hydrocarbon conversion

Table 2
n-pentane oxidation over VPO and VPBiO catalysts [a]

Catalyst	Concentration C_5 = 1.9 vol%					Concentration C_5 = 3.7 vol%				
	X (%)	selectivity (%)				X (%)	selectivity (%)			
		MA	PA	MMA	$C_{4=}$		MA	PA	MMA	$C_{4=}$
VPO-1	67	32	29	0	0	63	25	36	0	2
VPO-2	56	35	26	8	1	55	26	31	7	3
VPBiO-1	63	40	20	10	0	59	35	26	9	0
VPBiO-2	58	37	18	11	1	55	32	24	10	3

[a] Temperature 350°C, SV = 2400 h^{-1}, selectivity was calculated after C_5 conversion into a given product.
X – conversion; MA – maleic anhydride, PA – phthalic anhydride, MMA – citraconic anhydride; $C_{4=}$ – olefins.

and selectivity towards MA and MMA occurs, whereas the selectivity to PA increases.

4. Discussion

Results obtained in this work show that the introduction of overstoichiometric phosphorus and/or bismuth in VPO catalysts increases both the number of acidic surface centres A (see table 1), and the number of strong acidic centres. Since the binding energy of V 2p electrons in all the catalysts remains constant, it can be supposed, that the effective charge on vanadium atoms is unchanged. This conclusion and the observed rise of the surface P/V ratio can be considered as an evidence for the Brønsted type of these acidic centres, mainly present as (P-OH).

As follows from the SEM data (fig. 1), bismuth introduced into VPO catalysts is present in the form of a highly dispersed surface phase of bismuth phosphate. This observation agrees well with the results of XRD (see above) and XPS studies. XPS analysis showed, that the Bi/V ratio on the surface of both catalysts was higher than in the bulk (see table 1). This leads to the conclusion that this phase is preferentially concentrated on the surface. The BE values of Bi 4f electrons were much higher as compared to pure bismuth phosphate. This additional chemical shift can be due to the high dispersion of the bismuth compound. As it has already been shown [15], Bi–P–O compounds have rather high acidity. Therefore, introduced bismuth may contribute significantly to the observed increase of the V–P–O acidity (table 1).

It is known [16], that high acidity of a catalyst, especially strong acidity, favours the skeletal isomerization of hydrocarbons. Basing on the conclusions presented in this work it seems to be possible, by controlled modification of the surface composition of VPO catalysts, to realise a novel route for *n*-pentane partial oxidation directed to the formation of citraconic anhydride (see fig. 2, table 2). In this respect it should be noted, that the selectivity towards MMA (table 2) and both total number of acidic centres (A) and that of strong acidic centres (C/A) (table 1) change in the same sequence:

$$\text{VPO-1} < \text{VPO-2} < \text{VPBiO-1} < \text{VPBiO-2}.$$

This sequence has been determined for the catalysts in the conditioned form. However, distinct variations in the oxidation state of the catalysts surface can cause considerable loss of the selectivity to MMA.

Unfortunately, at present it is difficult to determine whether the *n*-pentane isomerization is an initial step of its oxidation process or if it proceeds just after *n*-pentane activation at the first and fourth carbon atoms. It can be rather expected that, as a result of the activation of the *n*-pentane molecule, an abstraction of a methyl group occurs which then is oxidized to CO_x (scheme 1).

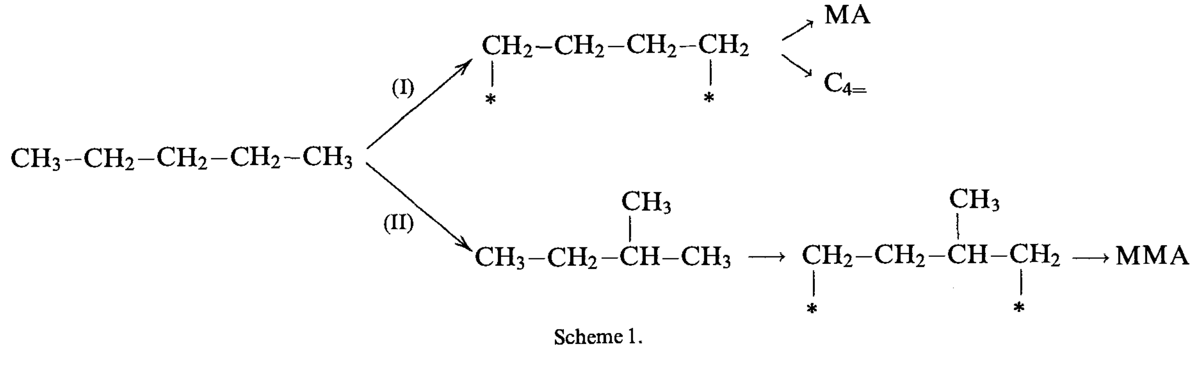
Along this route (I) containing terminal methylene groups, it is possible to realise two ways of further transformation: (i) into MA and (ii) into $C_{4=}$. The presence of the unsaturated terminal methylene group in the structure can lead also to its oxidation to C_4 aldehydes and acids. This possibility has been confirmed experimentally by mass-spectrometry (see lines with 72, 88 and 89 m.u. in fig. 2). The route (II) of the oxidation gives MMA.

In our opinion, PA is formed as the result of the condensation of maleic anhydride with C_4 olefins (butadiene):

$$\text{MA} + C_{4=} \rightarrow \text{PA}.$$

This idea is supported by the fact that a stronger isomerization function of the catalyst (higher acidity) is responsible for higher probability of the second route and as a consequence, decreases the selectivity towards PA (decrease of $C_{4=}$ forming probability) and increases that to MA (see VPO-1 and VPBiO-2 catalyst, table 2).

It should be emphasized, that the mechanism of the formation of PA through dehydrogenation of *n*-pentane to pentene, pentadiene and cyclopentadiene with generation of the templates, suggested earlier in refs. [8,9,17], has not been confirmed experimentally yet. During the oxidation of either pentene, pentadiene or cyclopentadiene the selectivity to PA was very low or equal to zero [17]. Also the oxidation of Br-pentane with the facilitated dehydrogenation function (but at C5 carbon atom) gave low selectivity to PA. Another disadvantage of this mechanism consists in the fact, that the *n*-pentane molecule adsorbs on oxides at the orientation parallel to the surface [18] and it is difficult even to imagine the formation of a spatial template. Additional crucial argu-



Scheme 1.

ments were provided by the study of the *n*-pentane oxidation by means of the TAP method [19]. The authors demonstrated that in this process, MA is formed before the PA peak appeared, and MA is responsible for the PA formation with the limitation of the process by C_4 olefins.

In conclusion, the mechanism of PA formation by dehydrogenation of *n*-pentane [8,9,17] seems to us less probable than the mechanism based on condensation of $MA + C_{4=}$ which is well supported by our experimental results and other reported data [19].

It has been shown in this study that citraconic anhydride may be obtained by partial oxidation of *n*-pentane. Basing on the experimental data, the reaction pathways of the formation of maleic and phthalic anhydrides have been suggested.

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