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Mechanochemistry: the activation method of VPO catalysts for *n*-butane partial oxidation

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Abstract

The paper describes the influence of the introduction of alkali and alkaline-earth metals into the VPO precursor and the effect of bismuth additive introduced into the VPO precursor by the mechanochemical treatment. XRD, XPS, DTA, TPD of NH_3 and determination of catalytic activity and selectivity in *n*-butane oxidation have been carried out. The preparations studied after mechanochemical treatment in a planetary mill were: (a) VPO, composed of $VOHPO_4 \cdot 0.5H_2O$, (b) VPBiO, containing the bismuth additive introduced during synthesis, (c) VPO/Bi_2O_3 and $VPO/BiPO_4$, mechanical mixtures of the VPO precursor and Bi_2O_3 or $BiPO_4$, respectively.

Introduction of alkali and alkaline-earth metals additives increases the basicity of surface oxygen in vanadium pyrophosphate, which entails increase in the rate of *n*-butane oxidation.

The mechanochemical treatment of the preparations changed their morphology, favouring the formation of the vanadyl (001) plane in the phosphate precursor. The XRD peaks of bismuth phosphate appeared instead of those of bismuth oxide and the +0.8 eV chemical shift in the XPS Bi4f band was observed. The change in the chemical state of VPO/Bi_2O_3 are an evidence of the occurrence of chemical reaction.

Mechanochemical treatment of $VPO/BiPO_4$ and VPO/Bi_2O_3 catalysts increases their activity in *n*-butane oxidation and the selectivity to maleic anhydride. Thus, mechanochemistry may be a promising method for introduction of promoting additives into the basic VPO composition.

Keywords: Mechanochemistry; Activation method; VPO catalysts; *n*-Butane oxidation

1. Introduction

Complex vanadium-phosphorus oxide systems are extensively used as catalysts in the process of the oxidation of *n*-butane to maleic anhydride. Introduction of promoting additives to the basic VPO catalyst is one of the methods to improve its catalytic properties [1–3].

However, little information is available on the character of changes in properties of the VPO system generated by the additives and the manner of their introduction. Even authors, who use the same method for catalyst preparation, express conflicting views on the influence of the same element on *n*-butane oxidation [4–7]. Therefore, studies of the role played by the nature of the additives, the method of their introduction and the phase in which they are present, are still in progress [8–12].

In our recent work [13] it was found that the

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additives may be present in four types of phases. It has also been shown, that among them, the most promising for improving catalytic properties of VPO compositions, is the case of additives which form ortho- or pyrophosphates. As an example, recently published results on Zn-addition [14] have confirmed the influence of the type of phase in which Zn is present, on the catalytic properties of VPZnO. Somewhat later [15] the positive effect of the addition of cobalt phosphate on the catalytic properties of $(VO)_2P_2O_7$ in *n*-butane selective oxidation has been demonstrated. Our prediction concerning the positive effect of the introduction of metal phosphate has recently been confirmed [16]. On the other hand it has been shown that mechanical milling changes the morphology and thereby may improve the catalytic properties [17,18].

It is well known that in the case of alkali and alkaline-earth metal additions, formation of bimetal phosphates and pyrophosphates, such as $Me^{I}VOPO_4$ and $MeVOP_2O_7$, may take place [19–25]. According to these data metal ions are distributed in empty channels of pyrophosphate or ortophosphate networks.

Early investigation of the properties of VPO catalysts containing alkali and alkaline-earth elements in the form of bi-metal phosphates have shown [9] that their activity is higher as compared to V P O samples but their selectivity to maleic anhydride falls to zero. Later, we have studied the effect of the addition of the same elements in small ($Me/V < 0.1$) concentrations on the properties of VPO ($P/V = 1$) catalyst [13,26] and found their beneficial influence. The influence of alkali and alkaline-earth elements on the properties of VPO catalysts was also studied in [27–31].

There exists another method of modifying the catalytic properties of VPO catalysts. Namely, mechanical milling has been also applied to change the morphology of catalysts and thereby to increase the catalytic activity [17,18].

Mechanochemical treatment of solids has been shown to modify not only their morphology and texture but to profoundly influence their reactivity, inducing solid state reactions to proceed in conditions in which otherwise the solids remain unreactive. It may be therefore considered as one of the prospective methods in solid state syntheses of new compounds [32,33].

In this paper we compare the changes in the properties of VPO compositions with a P/V ratio = 1.0 and 1.2, caused by introduction of Li, Na, K, Cs, Be, Mg, Ca, Ba and Bi at different concentrations, with those obtained by the application of mechanochemistry to both modification of morphology of catalysts and induction of surface transformations, in order to influence the activity and the selectivity.

2. Experimental

2.1. Samples

VPO catalysts were obtained by the known procedure [15,26] starting from V_2O_5 (pure for analysis, specific surface area $S_A = 4.5\ m^2/g$) and H_3PO_4 (87%) in *n*-butyl alcohol as a solvent (VPO catalysts, Table 1, Tables 2 and 3). Additives in the form of chlorides were introduced simultaneously with vanadium oxide. After precipitation, filtration and drying, the catalyst powder was used in other synthesis or wetted and extruded as pellets with 4.8 mm diameter and 5 mm length (Table 1, Tables 2 and 3).

In the mechanochemical studies VPO and VPO/Bi systems were investigated. Bi_2O_3 (Aldrich) and $BiPO_4$ (commercial) were used for the catalysts preparation.

Three types of the VPO/Bi catalysts were synthesized and studied. For synthesis of type one sample the bismuth additive was introduced in the form of $Bi(NO_3)_3\ 5H_2O$ into the solution simultaneously with V_2O_5 ($Bi/V = 0.1$) and H_3PO_4 ($P/V = 1.2$). This preparation will be denoted as VPBiO. The VPO/Bi_2O_3 (type two) and $VPO/BiPO_4$ (type three) ($Bi/V = 0.1$) samples were obtained by mixing in an agate mortar the powders of the VPO precursor and Bi_2O_3 or $BiPO_4$, respectively.

Table 1
Properties of the catalyst surface

Catalyst	Bulk ratio		Binding energy (eV)				Surface ratio		TPD (NH_3) [a]	
	P/V	Bi/V	O1s	P2p	$V2p_{3/2}$	$Bi4f_{7/2}$	$(P/V)_S$	$(Bi/V)_S$	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.

2.2. Pretreatment

The samples of the VPO and VPO/Bi series were mechanochemically treated in a planetary mill (3000 rpm) in air or in ethanol or water suspension. In the case of VPO/Bi, prior to catalytic tests, samples were activated in the reaction mixture for 60 h in the range 250–470°C with step-wise rise of temperature.

2.3. Analysis

Chemical analysis of vanadium and phosphorus content was performed in similar way as in [15]. Concentrations of additions were determined with the help of atomic-absorption spectrometer (Saturn-1).

The phase composition of the catalysts before and after their use in the reactor was analyzed using Toshiba powder and DRON-3M X-ray diffractometers with Cu K_α radiation.

The specific surface areas (S_A) of the samples were measured by the BET method on an ASAP-2000 and a Gasochrom-1.

The analysis of the surface composition was carried out by XPS on ES-100 Kratos and VG Scientific ESCA-3 spectrometers. The spectra (Al $K_{\alpha 1,2}$ excitation) were calibrated against C1s (284.8 eV) line as a standard in the binding energy determination. Details of the measurement and data processing are given in [15].

The composition of sub-surface layer and the in-depth profile in the pellets were obtained by means of scanning electron microscopy (Jeol: JSM-35 SF and JSM-35C) using an X-ray microanalyzer Ortek EEDS-II and 35-DDS (XMPA) following the procedure described in [15].

Also Nanoscope scanning tunnelling microscope was used for the investigation of morphology.

Catalytic properties of the synthesized samples towards oxidation of: n-butane (1.65 vol% in air) to maleic anhydride were examined. Catalytic tests were carried out in a flow reactor with chromatographic analysis of all products [26] for a range of $WHSV_s$ from 1500 to 6000 h^{-1}. The catalytic properties were compared for

Table 2
Surface properties (XPS) of the samples

Samples	Binding energy of electrons (eV)			$(P/V)_S$	$(Bi/V)_S$
	$V2p_{3/2}$	$Bi4f_{7/2}$	P2p		
VPO	517.5		133.9	1.43	
VPO/Bi_2O_3	517.5	158.9	133.9	1.47	0.09
VPO/$BiPO_4$	517.6	159.3	133.8	1.44	0.10
VPBiO	517.4	159.9	133.7	1.82	0.12
VPO/Bi_2O_3-MCh	517.6	159.7	134.0 136.7	2.02	0.00
VPO/$BiPO_4$-MCh	517.2	160.2	133.6	1.96	0.03
VPBiO-MCh	517.4	160.0	133.7	2.09	0.18

Table 3
Physical and chemical properties of the samples

Samples	XRD data		DTA data (°C)		S_A (m^2/g) [c]		n-Butane oxidation [d]		
	$I_{0.570}/I_{0.294}$	R_p (h^{-1}) [b]	T_{endo}	T_{exo}	BC	AC	SV (h^{-1})	X_C (%)	S_{MA} (%)
VPO	74/100	0.84	460	515	6.0	9.4	1800	73	67
VPO/Bi_2O_3	77/100	0.85	460	517	6.2	9.2	1800	66	63
VPO/$BiPO_4$	71/100	0.82	457	514	6.5	9.5	1800	68	64
VPBiO	88/100	0.85	450	508	5.7	8.7	2400	76	68
VPO/Bi_2O_3-MCh [a]	100/86	0.97	440	497	13.0	16.1	3000	83	71
VPO/$BiPO_4$-MCh [a]	100/87	0.96	435	490	13.5	16.5	3000	88	74
VPBiO-MCh	100/85	0.97	443	497	12.0	15.3	2400	79	70
VPO-MCh					8.8	11.4	1800	76	68

[a] MCh, sample after the mechanochemical treatment.

[b] R, ratio of the width at half of the peak maximum for the line $d = 0.294$ and 0.570.

[c] Specific surface area: BC, before and AC, after catalytic reaction.

[d] n-Butane oxidation at 440°C: SV, space velocity of the reaction mixture; X_C, n-butane conversion; S_{MA}, selectivity to maleic anhydride.

stationary characteristics obtained after not less than 48 h. Examination of catalysts for their stable operation was carried out in an element of the industrial unit (i.d. 25 mm, length of the catalyst bed 2.9 m) for 2000 h.

Acidity–basicity was determined by thermo-programmed desorption of NH_3 and CO_2 as test molecules. Oxygen mobility on catalyst surface was measured by thermo-programmed reduction of samples by hydrogen as described in [15].

3. Results

3.1. Precursor VPO

The XRD data show that all samples under investigation before catalytic tests contain the $VOHPO_4 \cdot 0.5H_2O$ phase. An excess of phosphorus in the samples practically does not cause any change in the pattern intensities. The analysis of 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.

3.2. Alkali and alkaline earth metal additives

Introduction of the additives to the VPO catalyst with P/V = 1.0 and 1.2 does not change the specific surface area, as compared to the basic VPO catalyst. The phase analysis shows, that after synthesis all precursors contain the $VOHPO_4 \cdot 0.5H_2O$ phase. Positions and intensities of X-ray lines were not affected by the presence of additives. After activation in the reaction feed all samples without any exception, contained the $(VO)_2P_2O_7$ phase.

The analysis of the content of additives in the sub-surface layer of catalysts after catalytic experiments (shorter than 80 h) by means of XMPA and on the surface by XPS were in good agreement with the results of chemical analysis representing their bulk concentrations. This can be taken as an evidence of the uniform distribution of additives in the catalyst. However, the P/V ratio shows the highest value at the surface, a little lower value in the subsurface layers, both being much higher than the bulk value. This indicates that surface enrichment of phosphorus takes place, its concentration decreasing on moving into the bulk. XPS spectra reveal also a tendency of the surface concentration of oxygen to increase with the introduction of alkali and alkaline-earth metals into the VPO catalyst.

Introduction of the additives in different concentrations did not cause any changes of the binding energy values of P2p- and $V2p_{3/2}$-electrons, while the binding energy of O 1s-elec-

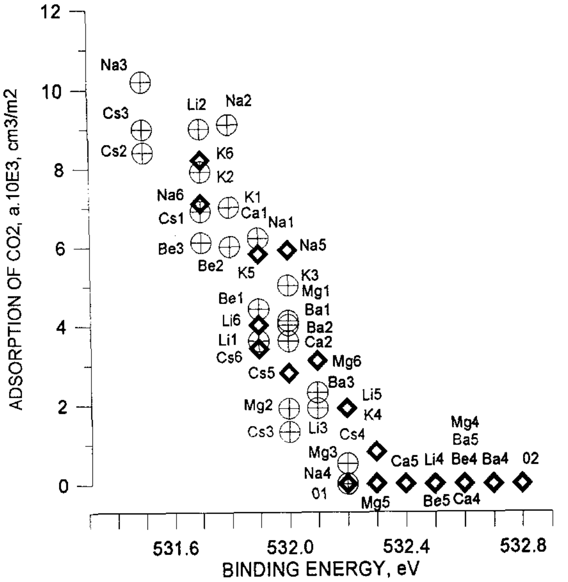

Fig. 1. The amount of CO_2 adsorbed on VPMeO catalysts as a function of the binding energy of O1s photoelectrons. The Me/V atomic ratio for (i) $P/V = 1.0$ catalysts (crossed circles): Me1 (0.02), Me2 (0.05), Me3 (0.10) and (ii) $P/V = 1.2$ catalysts (diamonds): Me4 (0.02), Me5 (0.05), Me6 (0.10). Catalysts without additives are marked as 01 and 02 respectively.

trons was reduced both in catalysts with $P/V = 1.0$ and that with $P/V = 1.2$. The decrease of binding energy of O 1s-electrons may be taken as evidence of the increase in the effective negative charge on oxygen atoms, corresponding to the increase of the basicity of the surface. This effect should result in significant adsorption of CO_2 which is not adsorbed on the unpromoted catalysts. Indeed, the amount of adsorbed carbon dioxide increased in good correlation with the decrease of the binding energy of O1s-electrons (Fig. 1).

It should be noted that the values of the binding energy of electrons in the introduced alkali and alkaline-earth metal cations are higher than those reported for their other simple compounds [34] Such binding energy shift, positive in all cases, may be caused by polarisation of metal atoms by strong electron acceptors like phosphorus and hydrogen, but to some extent it can be also due to high degree of the dispersion of additives.

3.3. Bismuth additives

The XRD data show that all samples before catalytic tests contain the $VOHPO_4 \cdot 0.5H_2O$ phase. Some additional lines observed, were attributed to the bismuth phosphate phase, in a good agreement with the literature data [35]. In the conditioned catalysts (n-butane oxidation for 80 h), besides the main phase of $(VO)_2P_2O_7$, bismuth phosphate lines were also observed.

At the VPBiO-2 catalyst surface, as revealed by scanning electron microscopy, beside the basic vanadyl pyrophosphate phase, another, different phase was also present. The study of the characteristic K_α-radiation from this part of the surface revealed minimum of the vanadium and the maximum of bismuth content. In contrast, phosphorus was uniformly distributed over the entire surface in every sample.

Results of the XPS study of the samples are given in Table 1 and 2. It can be noted that the binding energy (BE) of V2p and P2p electrons is practically unaffected by the sample composition. The BE of O1s-electrons slightly increased with the higher phosphorus content in the catalyst, whereas BE of Bi4f-electrons was measured significantly higher ($\Delta E = 0.9$–1.1 eV) as compared to the literature data for bismuth phosphate [36].

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 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.

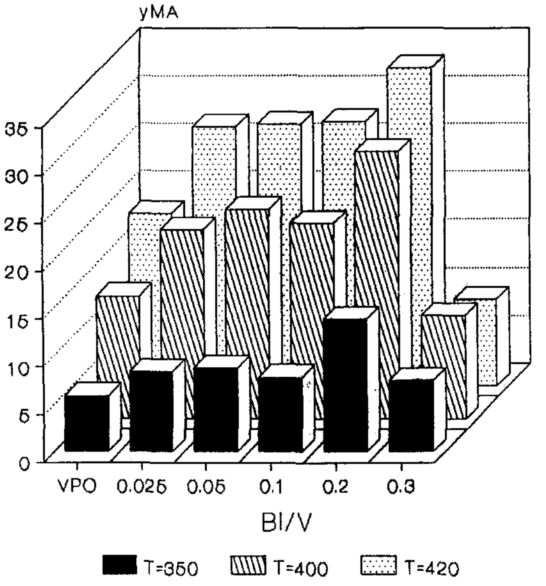

Fig. 2. Yield of maleic anhydride as a function of reaction temperature and Bi/V ratio in oxidation of *n*-butane over VPBiO catalysts.

Catalytic tests show (Fig. 2) that similarly to alkaline additives, also in the bismuth doped catalysts, the selectivity towards maleic anhydride passes through maximum at Bi/V = 0.2.

4. Discussion

4.1. Alkali and alkaline earth metal additives

The incorporation of elements which can easily donate electrons to the structure of vanadyl phosphate, should lead to an increase of an effective negative charge on oxygen atoms as compared to unpromoted catalyst, which indeed is confirmed in general by XPS. An increase of negative charge on oxygen should cause an increase of its basic properties, and as the consequence, CO_2 should adsorb on the catalyst surface, while it does not adsorb on the pure unpromoted VPO. Indeed, the amount of adsorbed CO_2 molecules (Fig. 1) increases with the increase of effective negative charge on oxygen (decrease of BE of O1s-electrons). We also found that the decrease of the BE of O1s-electrons on introduction of additives is accompanied by lowering of the temperature of the onset of reduction (T_{RO}). This effect may be due either to the accelerated activation of hydrogen by more basic oxygen, or to the decrease of lattice energy related to the substitution of low valent cations into the crystal lattice.

Introduction of additives causes also the increase of the rate of butane oxidation to maleic anhydride. The rate determining step of this reaction is the activation of butane through abstraction of a proton [13,15]. This step should be accelerated on increasing the basicity of surface oxygen atoms. This is indeed the case as illustrated by the linear dependence of the rate of butane oxidation on the BE of O1s-electrons (Fig. 3).

Introduction of alkali and alkaline-earth metals to the VPO catalyst causes an increase of surface P/V ratio [3,4]. A comparison of the results obtained by XPS and XMPA shows that the enrichment of surface with phosphorus occurs as the result of outward diffusion of overstoichiometric phosphorus through the pellet.

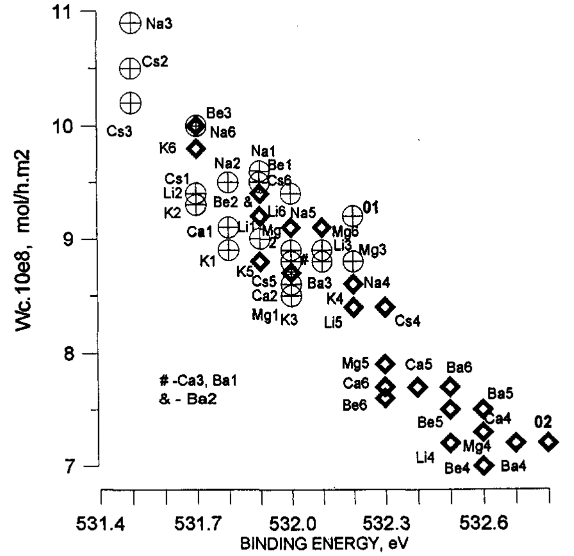

Fig. 3. The rate of *n*-butane oxidation on VPMeO catalysts in dependence on the surface basicity represented by the binding energy of O1s photoelectrons. For the catalyst composition see Fig. 1.

Such changes in surface composition lead to corresponding changes of acidic properties of the catalysts. The rise of phosphorus concentration on the surface is accompanied by simultaneous enrichment of the surface in oxygen [3,4].

Comparison of catalytic activity of samples with known surface acidity and basicity has shown that the rate of the reaction increases with the rising basicity of surface oxygen ions. Contrary to that the selectivity towards maleic anhydride is dependent on the amount of acidic centres at the catalyst surface, this dependence passing through a maximum.

It can be thus concluded, that additions of alkali and alkaline-earth elements to VPO composition can change both activity and selectivity of the catalyst.

4.2. Bismuth additives

Introduction of the overstoichiometric phosphorus and/or bismuth in VPO catalysts is increasing both the number of acidic surface centres A (see Table 1), and the number of strong acidic centres. Since binding energy of V2p-electrons in all 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 Bronsted type of these acidic centres, mainly present as (P–OH).

It follows from the XRD and XPS, that bismuth introduced into VPO catalyst is present in the form of highly dispersed surface phase of bismuth phosphate. XPS analysis showed, that the Bi/V ratios on the surface of both catalysts were higher than those in the bulk (see Table 1). This leads to the conclusion that this phase is preferentially concentrated on the surface. The BE values of Bi4f-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 [37], BiPO compounds have rather high acidity. Therefore, introduced bismuth may contribute significantly to the observed increase of the VPO acidity (Table 1).

4.3. Mechanochemistry

The data obtained show that mixing of VPO precursor with Bi_2O_3 or $BiPO_4$ powder (grinding in agate mortar) practically does not influence the properties of the basic $VOHPO_4 \cdot 0.5H_2O$ phase (Tables 2 and 3). The bismuth compounds, as was found by means of XRD and XPS studies, have remained in unchanged initial state, which was Bi_2O_3 and $BiPO_4$, respectively.

The introduction of bismuth into the catalyst during the synthesis (VPBiO sample) leads to slight decrease of specific surface area but intensity of the XRD peak at 0.570 nm (Table 3) and phosphorus surface concentration (Table 2) increase slightly. XRD spectra show that the additive is forming the bismuth phosphate phase. The binding energy of Bi4f-electrons in the VPBiO sample exceeds the value characteristic of bismuth phosphate (Table 2). This chemical shift of Bi4f-electrons, can be produced by a polarization of bismuth electrons due to its interaction with oxide ions of the vanadium phosphate matrix. Since such effects require a direct interaction in the atomic scale, it can be also taken as an indication of the fine dispersion of bismuth atoms, probably their incorporation into the basic $VOHPO_4 \cdot 0.5H_2O$ composition. The introduction of bismuth into the basic matrix during the precursor synthesis improves somewhat catalytic properties of the resulting catalyst.

The mechanochemical treatment of the samples caused a substantial increase of the 0.570 nm line intensity in XRD patterns which testifies to a relative growth of the exposure of vanadyl plane (001) in the precursor [38]. It is known [38,39] that the (001) plane of the $VOHPO_4 \cdot 0.5H_2O$ phase transforms into the topologically similar (100) plane of $(VO)_2P_2O_7$, which is believed to be responsible for the catalytic activity in *n*-butane oxidation [40,41].

The observed lowering of the phase transition temperature (Table 3) has also a beneficial effect on the formation of this plane. The observed gain of the parameter R_p demonstrates a decrease of the $VOHPO_4 \cdot 0.5H_2O$ plates thickness [42] and agrees well with the increase of the surface area of the samples mentioned above.

These results show that the precursor morphology is essentially affected by the mechanochemical treatment. Such changes can be connected with a sufficiently high local overheating ($\Delta T = 600–700°C$) appearing during the treatment, which can be capable to induce the chemical reactions and the synthesis of new compounds [43–45]. The fundamental changes in the state of VPO/Bi_2O_3 shown in this work are also an evidence of the proceeding of a chemical reaction. Namely, after the mechanochemical treatment the XRD peaks characteristic of bismuth phosphate appeared and those of bismuth oxide disappeared in the XRD patterns, while the binding energy of Bi4f-electrons increased by 0.8 eV and attained the value observed in the case of bismuth incorporated to $VOHPO_4 \cdot 0.5H_2O$ in the course of its preparation (VPBiO sample). This rise of chemical shift in XPS Bi4f band, indicates the change in the electronic state of bismuth atoms produced by a polarization of bismuth electrons as the result of its high dispersion in the vanadium phosphate matrix.

The comparison of the catalytic properties of the samples (Table 3) indicates that the mechanochemical treatment leads to the increase of both catalytic activity in *n*-butane oxidation and the selectivity towards maleic anhydride. The most efficient catalysts are $VPO/BiPO_4$-MCh and VPO/Bi_2O_3-MCh prepared by means of mechanochemistry from mechanical mixtures of $VOHPO_4 \cdot 0.5\ H_2O$ and $BiPO_4$ or Bi_2O_3. In the later case Bi_2O_3 transforms to $BiPO_4$. The catalytic performance of the VPBiO-MCh sample is a little worse probably due to the accumulation of the bismuth phosphate on the catalyst surface (cf. Table 2).

Thus, the results obtained show that bismuth added to the VPO catalysts, is finely dispersed improving the catalytic performance in *n*-butane partial oxidation. The mechanochemical treatment of VPO preparations, containing bismuth, changes the morphology of the precursor, favouring the formation of the (001) plane with the exposed vanadyl oxygen atoms. The data obtained for $VPO/BiPO_4$ and VPO/Bi_2O_3 samples demonstrate that the mechanochemistry is a new promising method for introduction of promoting additives into the basic VPO composition.

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