# The influence of the metal ions modification on physic-chemical properties of VPO catalyst in *n*-pentane oxidation

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**Introduction.** VPO catalysts are known as the catalytic systems for selective transformation of inert paraffins [1], particularly *n*-butane to maleic anhydride (MA) and *n*-pentane to maleic and phthalic anhydrides (PhA) at al. A development of catalytic properties of the VPO composition is possible by means of the introduction of additives of a various nature **.**

**Experimental.** Basic VPO composition and VP*Me*O samples modified by ions of *Me*=Bi, La, Mo, Te, Fe, W, Zr, Ti, Ag, Ni were synthesized in organic solution medium of n-butanol with $V_2O_5$ and $H_3PO_4$ (the atomic ratio P/V=1.15 and *Me*/V=0.05-0.40) by known method [2]. The synthesized samples were investigated by means of X-ray phase analysis (XRD), X-ray photoelectron spectroscopy (XPS), differential thermal analysis (DTA), scanning electron microscopy (SEM). Types of acidic centers on the VP*Me*O surface were defined by dimethylpyridine and 2,6-dimethylpyridine adsorption methods.

**Results.** The XRD data show that all the investigated samples before activation in the stream of reactant contained the $VOHPO_4 \bullet 0.5H_2O$ precursor phase. VPMoO patterns are the exception in which the $(NH_4)_3PO_4MoO_3$ phase are forming with character reflections. Results of DTA show an influence of additives on the crystallization stage of $(VO)_2P_2O_7$ phase in VP*Me*O samples. SEM data of VP*Me*O patterns show that all additives have the effect on morphology of VPO matrix. XPS results show introduction of additives changes O 1S-electrons binding energy. This fact can influence on the rate of paraffin transformation. The additives introduction influences on acid-base properties of the surface of VP*Me*O catalysts. It was established that a change of these properties regulates the selectivity of anhydrides, particularly the selectivity of PhA and MA formation in partial oxidation of *n*-pentane.

***Fig. 1. XRD patterns of VPMeO samples at Me/V≤0.10; + $VOHPO_4 \bullet 0.5H_2O$ phase.***

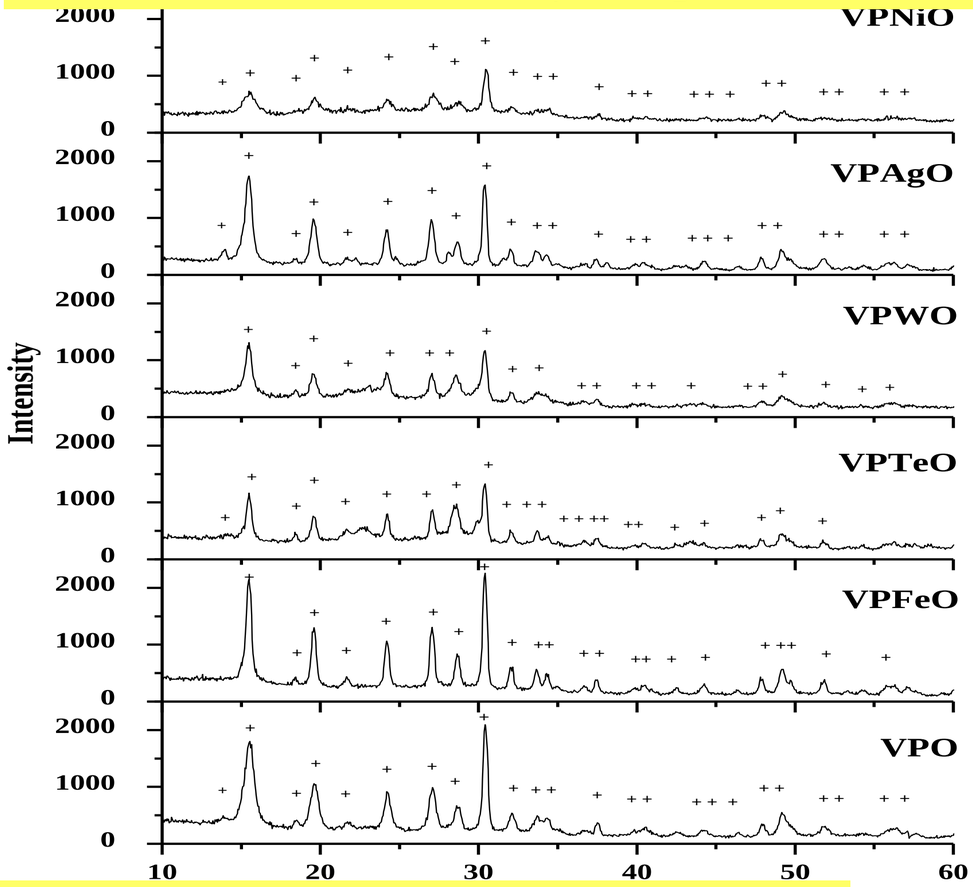



***Table 1. The data of DTA analysis of the promoted samples.***

| | 117-177 °C | 440-487 °C | 510-697 °C | 594-777 °C |
|---|---|---|---|---|
| $VOHPO_4 \bullet 0.5H_2O$ → | $2VOHPO_4$ | →$(VO)_2P_2O_7$}amorphous → | {$(VO)_2P_2O_7$}crystal → | $2VOPO_4$ |

| Sample | Me/V | Temperature effect, °C | | | |
|---|---|---|---|---|---|
| | | I endo | II endo | I exo | II exo |
| VPO | - | 145 | 465 | 567 | 644 |
| VPMoO | 0,10 | 125 | 450 | 610 | 657 |
| VPFeO | 0,10 | 139 | 474 | 577 | 727 |
| VPWO | 0,10 | 135 | 475 | 687 | 777 |
| | 0,20 | 137 | 467 | 697 | 771 |
| VPTeO | 0,10 | 135 | 472 | 572 | 650 |
| | 0,20 | 137 | 476 | 567 | 648 |
| VPTiO | 0,10 | 130 | 470 | 554 | 657 |
| VPLaO | 0,20 | 124 | 487 | 590 | 627 |
| VPBiO | 0,10 | 136 | 428 | 517 | 740 |
| VPZrO | 0,10 | 117 | 438 | 540 | 664 |
| | 0,20 | 152 | 444 | 520 | 697 |
| VPNiO | 0,18 | 171 | 440 | 510 | 594 |
| VPAgO | 0,10 | 165 | 444 | 530 | 627 |
| | 0,20 | 177 | 446 | 531 | 631 |

***Fig. 2. Scanning electron microphotographies of VPMeO samples at Me/V=0.10 atomic ratio and the element distribution.***

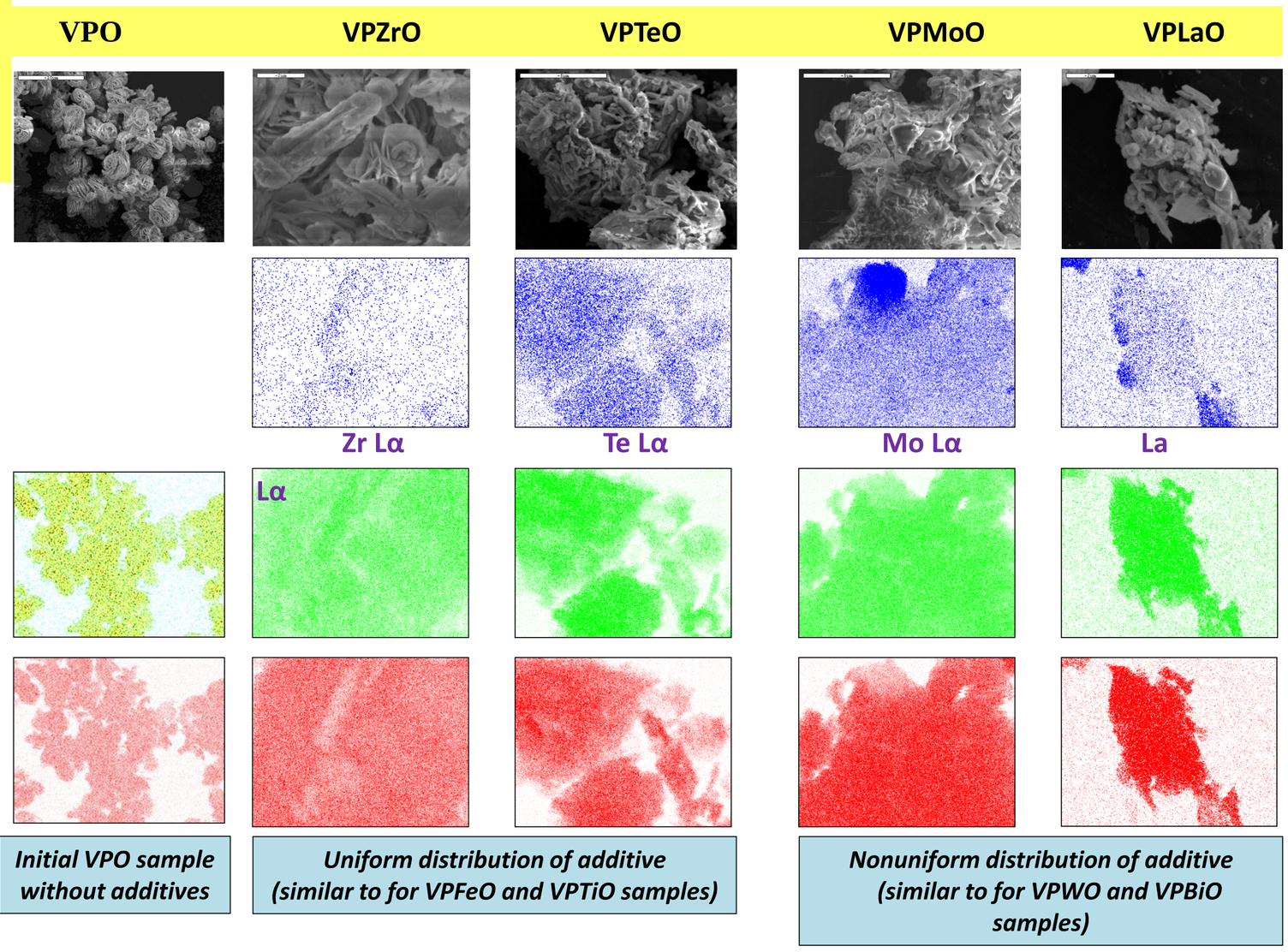
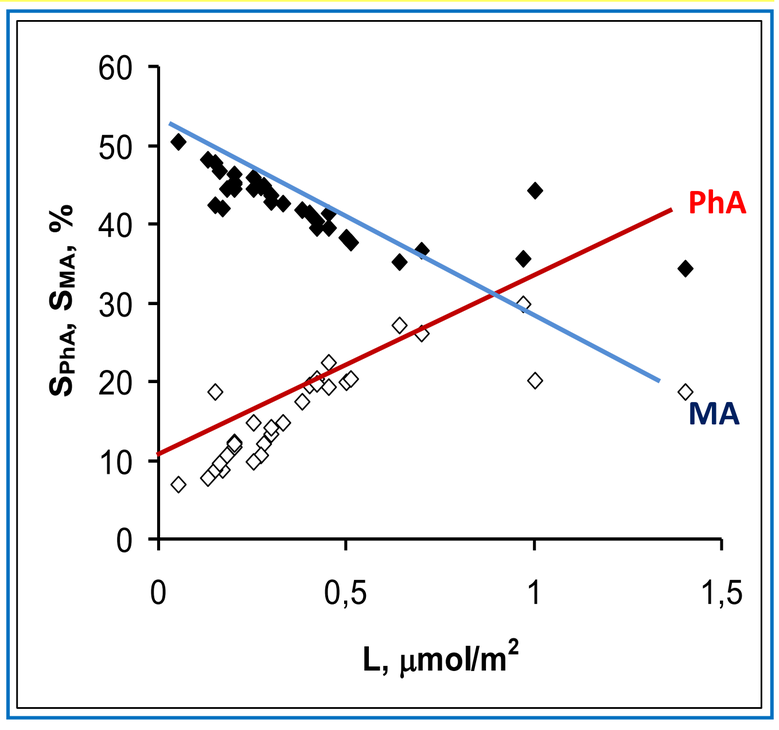



***Fig. 3. Selectivity to MA and PhA in n-pentane oxidation from Lewis acidity of surface of VPMeO catalysts.***




**References**

1. *Centi G., Golinelli G., Busca G.* Modification of the surface pathways in alkane oxidation by selective doping of Bronsted acid sites of vanadyl pyrophosphate // J Phys Chem. - 1990. - **94**. - P. 6813-6819.
2. *Zazhigalov V.A., Haber J., Stoch J. et al.* Properties of cobalt-promoted $(VO)_2P_2O_7$ in the oxidation of butane // Applied Catalysis. – 1993. – **96**. – P. 135-150.