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"CATALYSIS: FUNDAMENTALS AND APPLICATIONS"

Reaction Mechanism–Based Design of Efficient VPO Catalysts for n-C_5H_{12} Oxidation into Phthalic, Maleic, and Citraconic Anhydrides

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Abstract—Hypotheses as to possible ways of enhancing the selectivity of partial *n*-pentane oxidation with respect to phthalic, maleic, and citraconic anhydrides are suggested based on the mechanistic concepts of the formation of these products. The hypotheses are checked by studying the properties of vanadium–phosphorus oxide (VPO) catalysts upon the introduction of different concentrations of La, Bi, Fe, W, Te, Ti, Zr, or Mo. It is shown by various physicochemical methods (x-ray diffraction, IR spectroscopy, X-ray photoelectron spectroscopy, and pyridine and 2,6-dimethylpyridine adsorption) that the phase composition of the VPO catalyst and the oxidation states of its elements on the surface are not changed in most cases upon the introduction of these additives. The additives mainly affect the number of Lewis acid sites, whereas the Brønsted acidity changes only slightly. The existence of a correlation between the citraconic anhydride selectivity and the total acidity of the modified catalyst surface is confirmed. In agreement with the assumptions as to the process selectivity, it was discovered that the phthalic anhydride selectivity increases with an increase in the number of Lewis acid sites. The observed regularities open up the way to the purposeful synthesis of catalysts with enhanced selectivity with respect to these products.

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INTRODUCTION

The synthesis of catalysts capable of selectively leading the process toward the desired partial oxidation product is an interesting and important task of catalysis science. The solution of this problem can be based on the knowledge of the process mechanism, which would make it possible to pass from randomly choosing catalysts to purposefully synthesizing catalysts with definite physicochemical properties.

An interesting object for such a study is the partial oxidation of n-C_5H_{12}, which yields three products: phthalic anhydride (PA), maleic anhydride (MA), and citraconic (CA) anhydride. The process was considered as an alternative to the commercial synthesis of PA by *ortho*-xylene oxidation. The reaction occurs in the presence of vanadium–phosphorus oxide (VPO) catalysts. Although the first results [1–3] showed that a high PA selectivity can be achieved, no confirmation was obtained in later studies [4–9]. The introduction of Co or Fe into the base VPO catalyst [10] did not increase the PA yield, and only Bi [11] exerted a favorable effect.

We suggested a mechanism for the formation of the products of *n*-pentane partial oxidation on the VPO catalysts [7, 11, 12]. The proposed scheme allowed some assumptions to be made as to possible routes of the synthesis of the catalysts with enhanced performance parameters with respect to the partial oxidation products [11, 12]. According to these assumptions, an increase in the total acidity of the catalyst should result in an increase in the probability of linear paraffin isomerization and in the corresponding increase in the CA selectivity. The formation of PA by the Diels–Alder reaction between maleic anhydride and the intermediate diolefinic structure is limited by the low steady-state concentration of the latter. An increase in the steady-state concentration of the intermediate diolefinic structure and the corresponding increase in the PA selectivity can be achieved by increasing the number of Lewis acid sites on the VPO catalyst surface. This would also decrease the MA selectivity.

Based on these assumptions, one can control the selectivity of formation of each anhydride during *n*-pentane oxidation by changing the acid properties of the surface. To check this possibility, we studied the modification of the properties of the base VPO composition by additives of different natures, varying their amounts in the catalyst. We used modifying elements (Table 1) with different electronegativities [13] in order to achieve substantial changes in the acid properties of the base VPO catalyst.

EXPERIMENTAL

The VPMO catalysts (M = La, Zr, Ti, Bi, Fe, Mo, Te, W) were synthesized in butanol according to a known procedure [11]. The additives as salts were introduced into the synthesis simultaneously with vanadium oxide. The M/V atomic ratio was varied between 0.05 and 0.40 (Tables 1, 2), while the P/V ratio was fixed at 1.15.

The synthesized VPMO samples were characterized by physicochemical methods. X-ray diffraction (XRD) analysis was carried out with a DRON-3M instrument using filtered CuK_α radiation (λ = 0.15418 nm). IR spectra were recorded as KBr pellets on a Specord M80 spectrophotometer. The catalysts were examined by scanning electron microscopy with a Hitachi S-4000 instrument using an accelerating voltage of 5 kV. The catalyst surface was studied by X-ray photoelectron spectroscopy (XPS) with a VG ESCA-3 spectrometer using monochromatized AlK_α radiation (1486.6 eV). Electron binding energies were calibrated against the C 1*s* line (284.8 eV). The specific surface area was determined from nitrogen thermal desorption data using a Gazokhrom-1 instrument. The acid properties of the surface were characterized by the amounts of adsorbed pyridine and 2,6-dimethylpyridine. Those were determined chromatographically: the column was filled with the sample examined, and pulses of one reactant or another were injected into the column using a dosage valve. This method [14] makes it possible to determine the total acidity of the sample (*A*) from the amount of adsorbed pyridine, and the number of Brønsted acid sites (*B*) can be calculated from 2,6-dimethylpyridine adsorption. The number of Lewis acid sites was determined as the difference *A*–*B*.

The catalytic properties of the synthesized VPMO samples were studied using a flow-type setup with a stainless steel reactor (internal diameter of 6 mm). Samples to be examined were pressed and crushed. The 0.25–0.50 mm size fraction was loaded into the reactor (the catalyst volume was 0.5 cm^3). The catalytic reaction conditions were the following: reaction mixture composition, 1.80 vol % n-C_5H_{12} + air; volumetric flow rate, 12–46 cm^3/min; T = 200–420°C. The reaction products were analyzed by gas chromatography using a flame-ionization detector (FID) and a thermal conductivity detector (TCD) as described earlier [12].

RESULTS AND DISCUSSION

The XRD data presented in Fig. 1 show that the additives do not change the phase composition of the initial VPO catalyst if the M/V atomic ratio does not exceed 0.1, regardless of the nature of the introduced additive. An increase in the additive content of the base VPO composition (M/V > 0.1) results in several effects. As shown in Fig. 2, an increase in the iron content of the catalyst leads to its amorphization. A similar partial amorphization of the sample is caused by Te at Te/V = 0.2 and by W at W/V = 0.3. As was shown previously [11], an increase in the bismuth content of the VPO catalyst results in the appearance of reflections from the $BiPO_4$ phase, which coexists with the main crystalline phase VPO. A similar effect is caused by lanthanum (Fig. 3). The data in Fig. 3 show that an increase in the lanthanum content increases the intensity of the reflections from $LaPO_4$ and reduces the relative intensity of the reflections from the base phase VPO. At Mo/V = 0.3, new reflections appear at d = 0.824, 0.412, 0.336, 0.291, 0.248, 0.189, 0.176, 0.165, and 0.143 nm, which are characteristic of the $(NH_4)_3PO_4(MoO_3)$ phase. For the other additives, no changes in the X-ray diffraction pattern were observed upon an increase in the additive content. Thus, vanadyl phosphate is the major crystalline phase in most of the catalysts examined. This finding is essential for correct correlation of physicochemical and catalytic properties in light of the earlier report that vanadyl phosphate crystal modification affects the activity and selectivity of the catalyst in paraffin oxidation [15].

Table 1. Additives introduced into the base VPO catalyst

Additive (M)	Electronegativity		Range of M/V atomic ratios
	Pauling	Sanderson	
La	1.1	1.39	0.10–0.40
Zr	1.4	1.63	0.05–0.20
Ti	1.6	1.66	0.05–0.20
Bi	1.8	1.93	0.05–0.30
Fe	1.8	2.28	0.05–0.40
Mo	2.1	2.14	0.10–0.30
Te	2.1	2.24	0.05–0.20
W	2.1	2.86	0.05–0.30

Calculations using the Scherrer equation demonstrate that the particle size of the additive-containing catalysts is somewhat larger than that of the base VPO composition (Table 2). At the same time, no regular relationship is observed between the amount of additive introduced and the particle size of the main phase. The observed changes in the vanadyl phosphate particle size can hardly affect the catalytic properties. The data presented in Table 2 show that the additives change the specific surface area of the base VPO material. For instance, the introduction of any amount of La, Zr, or Ti increases the specific surface area of the catalyst. The Mo and W additives increase this value only at a high content. The other additives decrease the specific surface area of the VPO catalyst. Our results suggest no regular correlation between the amount of the additive and the specific surface area of the catalyst.

The data presented in Fig. 4 show that introducing additives into the base VPO sample and raising their content exert no significant effect on the IR spectrum. The spectra exhibit absorption bands at 413–417 (δ P–O), 675–687 (δ V–O–P, δ O–V–O), 975–976

Table 2. Properties of the VPMO catalysts

Sample	Atomic ratio M/V	SSA, m^2/g	Particle size, nm	Electron binding energy, eV	
				V 2*p*	P 2*p*
VPO	–	15.1	9.9	517.2	133.8
VPLaO	0.10	16.9	14.2	517.6	133.4
	0.20	19.6	15.1	517.6	133.5
	0.40	31.3	14.0	517.1	132.9
VPZrO	0.05	19.5	15.9	517.3	133.5
	0.10	23.0	13.1	517.3	133.6
	0.20	18.0	13.9	517.2	133.6
VPTiO	0.05	15.0	10.5	517.4	133.8
	0.10	22.0	12.1	517.3	133.9
	0.20	16.0	11.7	517.4	133.6
VPBiO	0.05	12.2	19.9	517.1	133.7
	0.10	11.4	17.2	517.2	133.8
	0.20	12.2	15.6	517.4	133.9
	0.30	12.8	15.7	517.3	133.7
VPFeO	0.05	7.8	18.3	517.2	133.6
	0.10	8.4	14.5	517.5	133.9
	0.20	9.5	w.n.d.	517.6	133.9
	0.30	6.5	w.n.d.	517.7	133.6
	0.40	9.3	w.n.d.	517.5	133.5
VPMoO	0.10	14.0	16.3	517.5	133.7
	0.20	14.1	14.2	517.3	133.7
	0.30	36.5	10.5	517.3	133.7
VPTeO	0.05	8.8	23.9	517.3	133.6
	0.10	10.5	13.9	517.4	133.7
	0.20	9.5	w.n.d.	517.2	133.7
VPWO	0.05	6.0	19.8	517.3	133.9
	0.10	6.0	19.2	517.3	133.9
	0.20	16.0	18.0	517.3	134.0
	0.30	25.4	w.n.d.	517.4	134.0

Note: w.n.d. = was not determined.

(ν V=O), 1050–1194 (ν PO_3), 1381–1382 (δ P–OH), and 1631–1637 (δ H–O–H) cm^{-1}, which are characteristic of vanadyl phosphates [16–21]. The intensities of these bands decrease with an increase in the amount of the phosphate-forming additives (see above). The IR data confirm the X-ray diffraction data for the samples

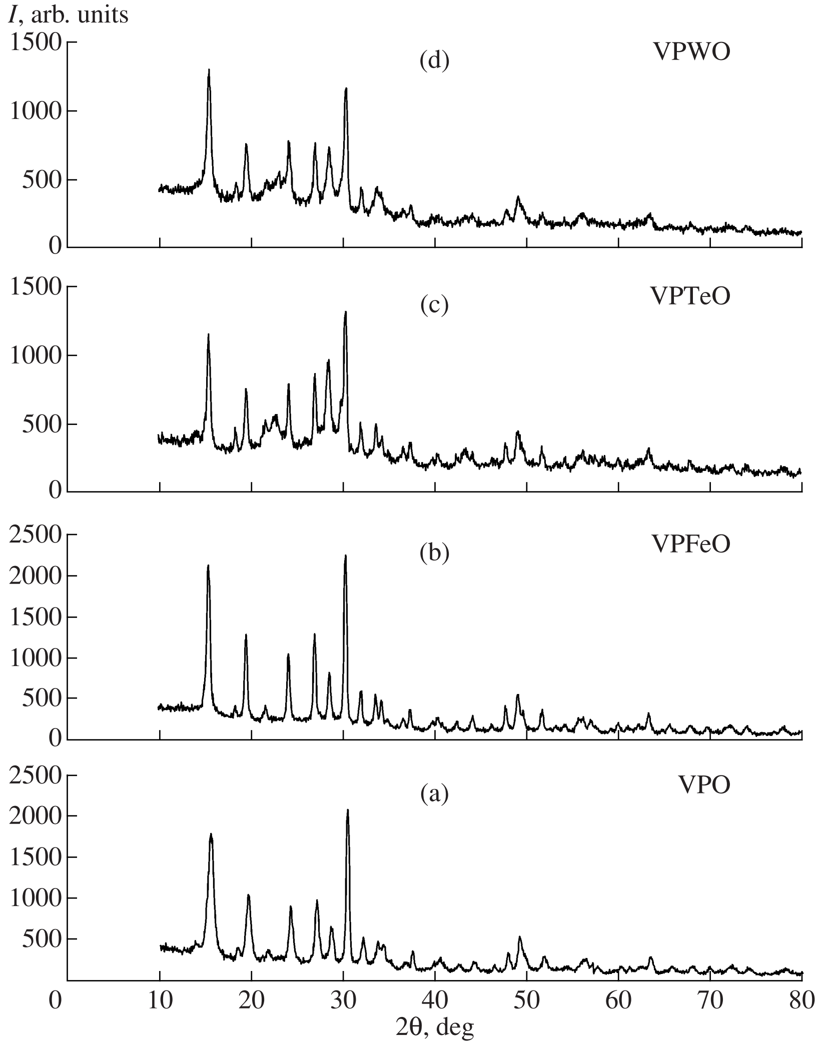

Fig. 1. X-ray diffraction patterns from (a) the VPO catalyst and (b–d) VPMO catalysts with M/V = 0.5 and M = (b) Fe, (c) Te, and (d) W.

and indicate that the base VPO phase remains unchanged. These results suggest that the disappearance of the phosphate vanadyl reflections observed at some additive concentration (see above) is due to the decrease in the crystallite size, while the structure of the main phase remains unchanged.

Typical SEM data for the catalysts are presented in Fig. 5. As can be seen from the micrographs obtained using the characteristic radiation of vanadium and the additive elements, there are two types of additive distributions in the base VPO composition. Like iron (Fig. 5), zirconium, titanium, tellurium, and tungsten are uniformly distributed in the base VPO catalyst. In the case of lanthanum (Fig. 5), bismuth, or high molybdenum contents, the additive concentration is increased in some areas of the sample, the vanadium concentration is decreased, and the phosphorus distribution remains uniform, confirming the formation of phosphates of the elements introduced. Thus, the SEM data confirm the XRD data concerning the distribution of the additives in the base VPO material.

XPS data for the synthesized samples are listed in Table 2. The additives exert only a slight effect on the binding energies of the V $2p_{3/2}$ and P $2p$ electrons. Therefore, the oxidation states of V and P on the catalyst surface remain invariable. These results possibly indicate that the phase composition of the catalyst is unchanged. According to XPS data, the surface P/V ratio increases in all cases upon the introduction of an additive, indicating that the catalyst surface is enriched with phosphorus. A similar situation was observed earlier upon the introduction of additives of another nature into the VPO catalyst (see, e.g., [22–25]).

Thus, the above results suggest that the additives examined exert no effect on the phase composition of the base VPO material or on the valence state of the elements on the catalyst surface. This is significant for cor-

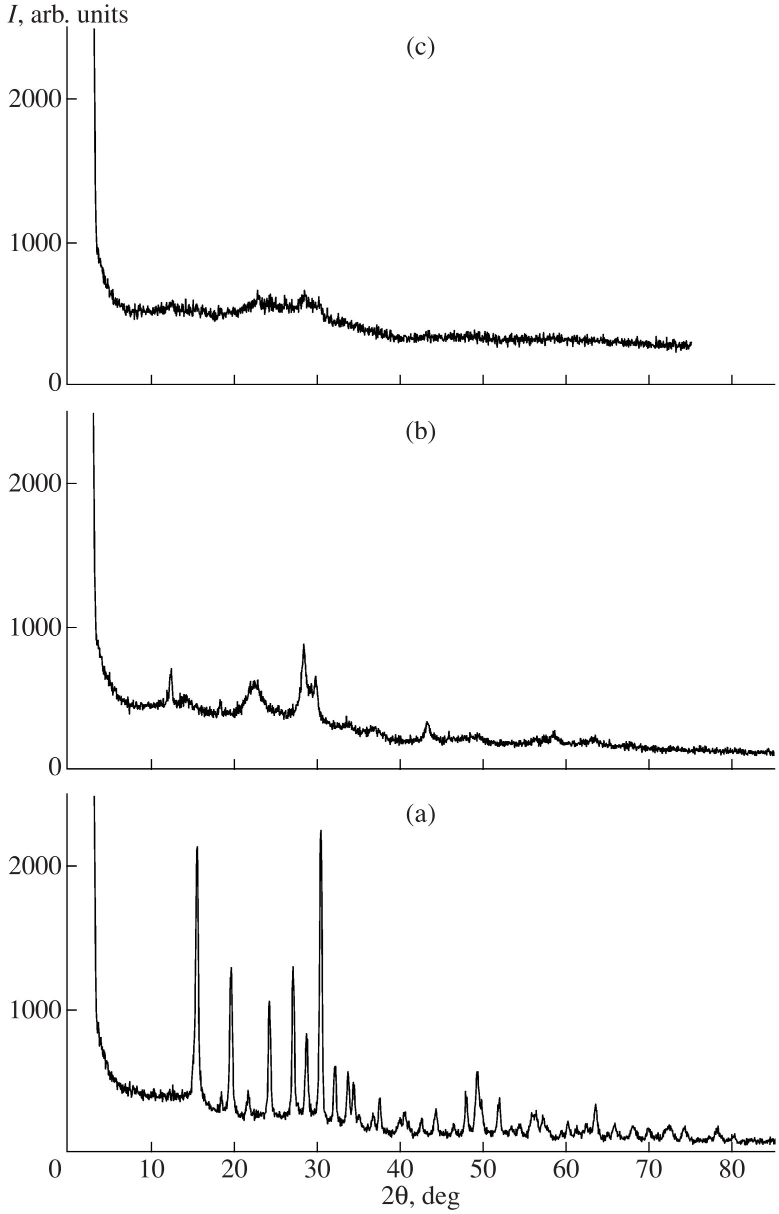

Fig. 2. X-ray diffraction patterns from VPFeO catalysts with Fe/V = (a) 0.05, (b) 0.2, and (c) 0.4.

rectly correlating the anhydride formation selectivity data for *n*-pentane oxidation with the acid properties of the surface of the modified catalysts and for verifying the assumption that understanding of the process mechanism provides a means of controlling the performance of the catalyst.

The surface acid properties of the catalysts were studied by measuring the amounts of adsorbed pyridine (the total number of Brønsted and Lewis acid sites, i.e., the total acidity) and 2,6-dimethylpyridine, which is adsorbed only on Brønsted sites. The plots of the amount of adsorbed pyridine versus the additive content of the sample are shown in Fig. 6. As follows from these results, two groups of catalysts can be distinguished. For the first group, we observe a peaking dependence of the number of acid sites on the additive content. This group includes the catalysts in which the additive forms a phosphate phase (La, Bi) and the catalysts in which the base VPO material is partially amorphized. The second group consists of the VPO catalysts in which the additives do not exert any significant effect on their phase composition. In these catalysts, the concentration of acid sites increases steadily with increasing additive content. The much higher acidity of the Mo-containing sample with Mo/V = 0.3 can be due to molybdenum phosphate formation, as was shown

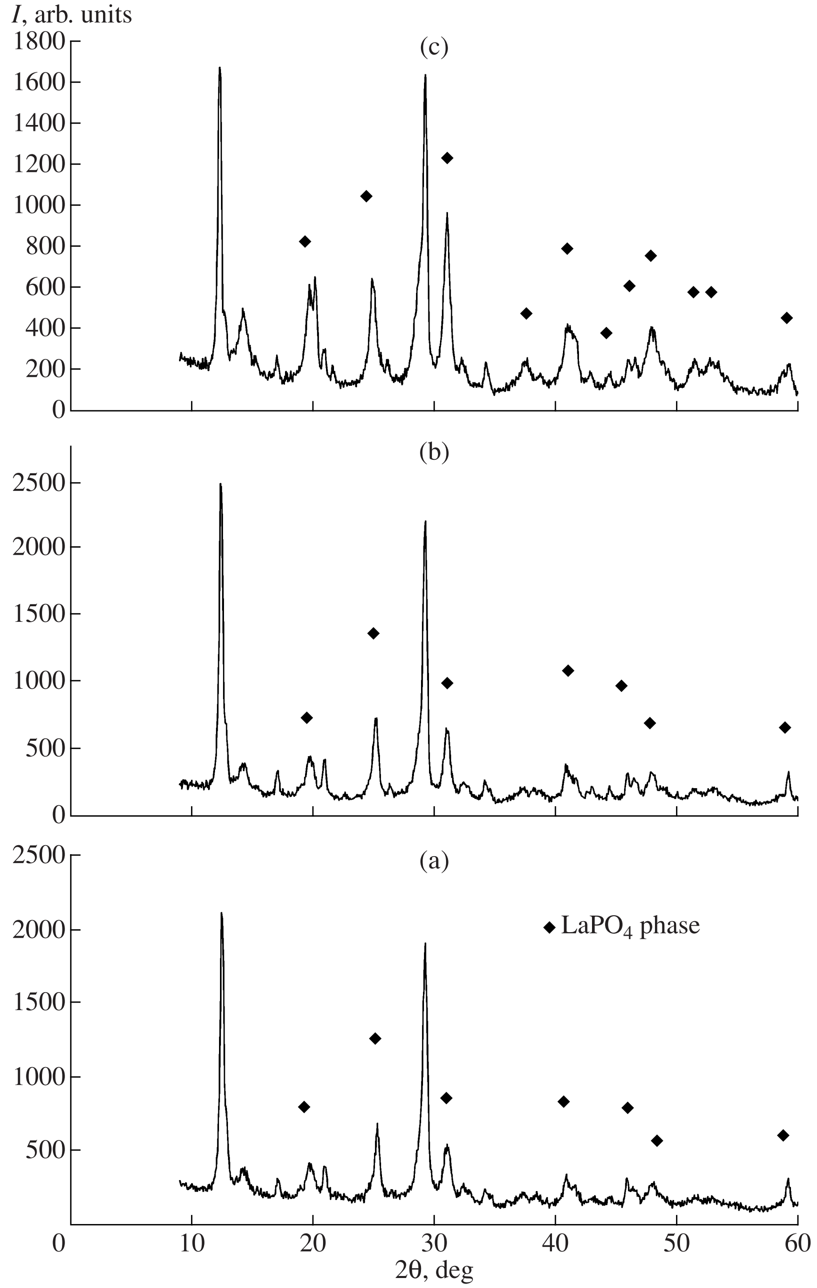

Fig. 3. X-ray diffraction patterns from VPLaO catalysts with La/V = (a) 0.1, (b) 0.2, and (c) 0.4.

above. Note that the increase in the acid site content is greater for the first group (and for the VPOMo sample with Mo/V = 0.3) than for the second group.

The dependence of the amount of adsorbed 2,6-dimethylpyridine on the additive content of the VPO catalysts is presented in Fig. 7a. As can be seen, the number of Brønsted acid sites is changed insignificantly by the additives. A slight increase in the Brønsted acidity is observed only as the iron or tungsten content is increased. The exception is the lanthanum-containing catalyst, for which the number of Brønsted acid sites increases substantially at La/V = 0.1.

These results are somewhat unexpected because it was found by XPS that additives increase the surface P/V ratio (see above). However, the data presented in Fig. 7b show no dependence of the Brønsted acidity on the surface P/V ratio (according to XPS data) for a given additive content of the catalyst. Since the Brønsted acidity depends primarily on the number of P–OH groups, it is likely that excess phosphorus on the surface forms P–O–M groups or exists as $(P_2O_5)_n$ con-

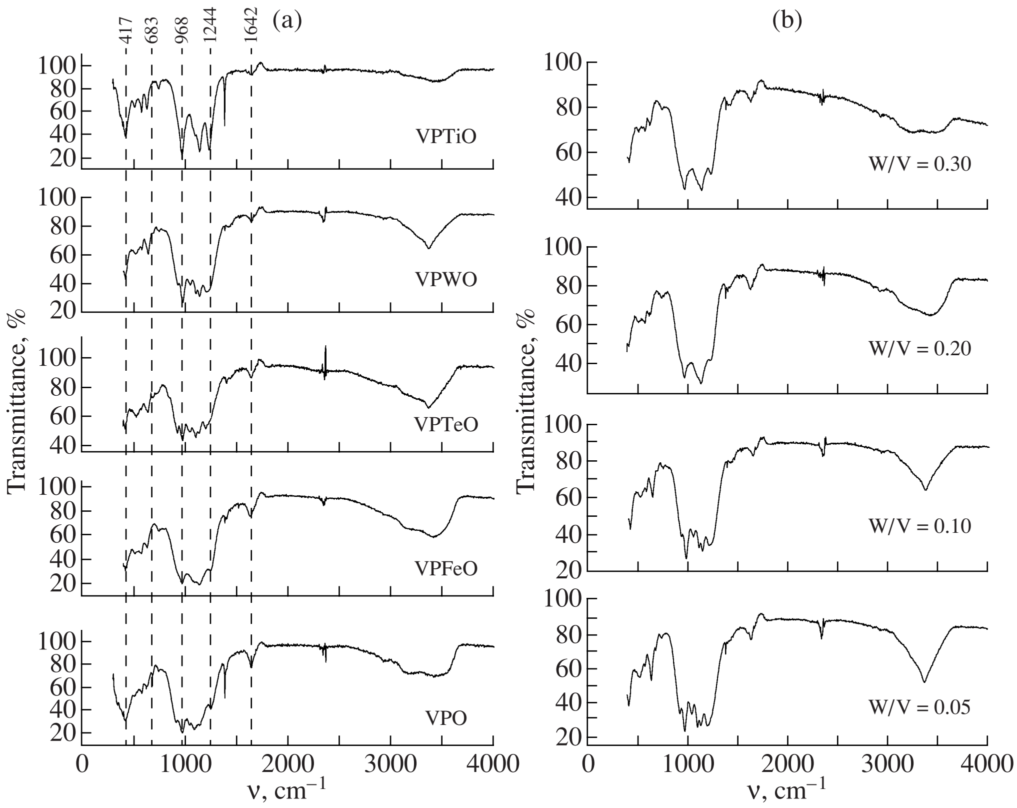

Fig. 4. IR spectra of the (a) VPMO and (b) VPMO catalysts.

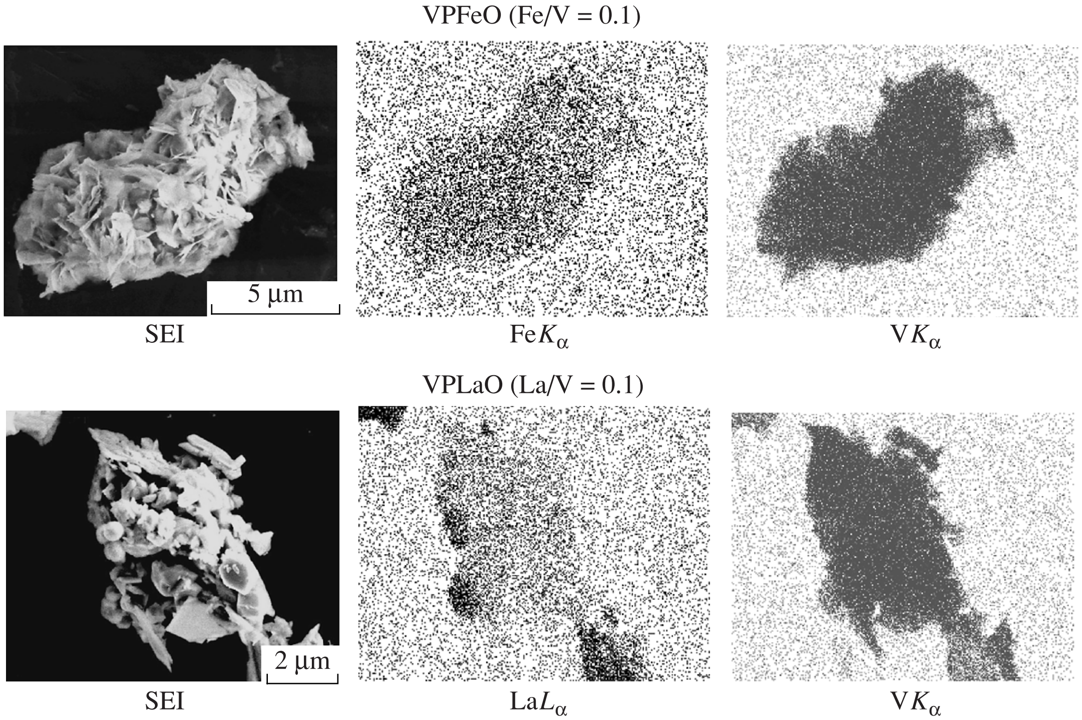

Fig. 5. Electron micrographs of the VPMO catalysts obtained in the secondary electron imaging (SEI) mode and using characteristic V radiation (VK_α), including iron (FeK_α) and lanthanum (LaL_α) additives.

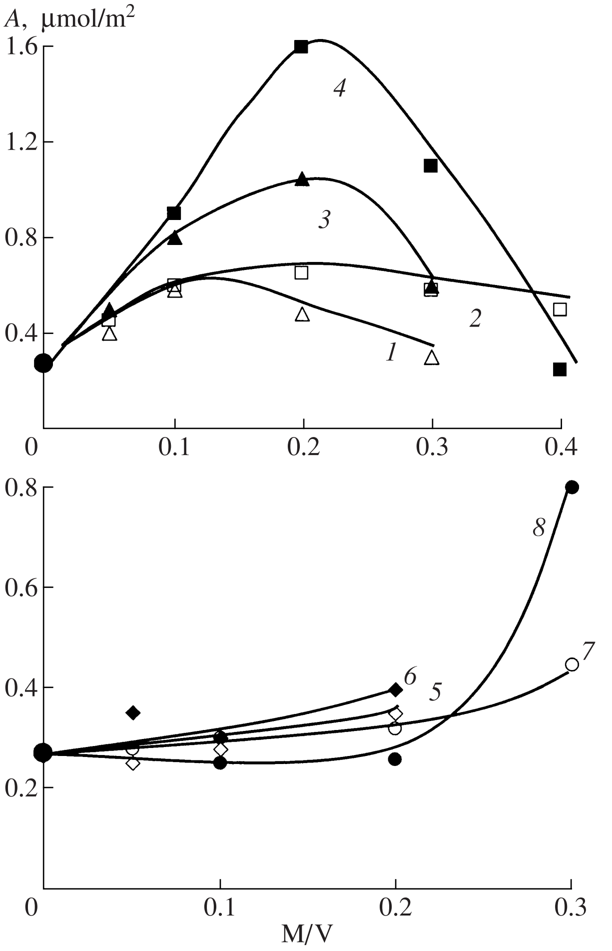

Fig. 6. Plots of the amount of adsorbed pyridine versus the additive content of the VPMO catalyst for M = (*1*) W, (*2*) Fe, (*3*) Bi, (*4*) La, (*5*) Zr, (*6*) Ti, (*7*) Te, and (*8*) Mo.

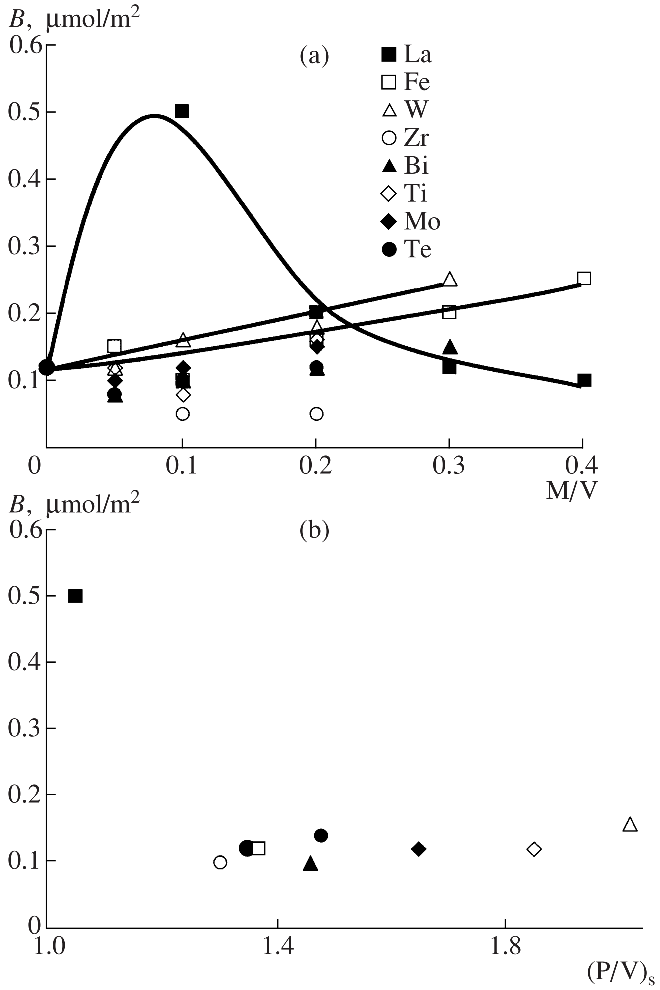

Fig. 7. Plots of the amount of adsorbed 2,6-dimethylpyridine (*B*) versus (a) the additive content of the VPMO catalyst and (b) the P/V ratio on the (*1*) VPO and (*2*) VPMO catalyst surface at M/V = 0.1 and M = La, Fe, W, Zr, Bi, Ti, and Te.

densed groups, as was assumed in [26, 27]. As a consequence, the number of P–OH groups does not increase and the additives affect the Brønsted acidity only slightly.

The dependence of the number of Lewis acid sites (total acidity minus Brønsted acidity) on the additive content of the catalysts is shown in Fig. 8. As can be seen, this dependence is qualitatively the same as the dependence of the total acidity on the additive content (Fig. 6). Two groups of catalysts can be distinguished here, namely, catalysts whose acidity peaks at some M/V value and catalysts whose acidity grows steadily throughout the additive content range. Either group consists of the same additive elements as in the case of the change in the total acidity of the samples.

Thus, our results demonstrate that the introduction of additives of different natures makes it possible to change the acid properties of the VPO catalyst surface without changing its phase composition or the oxidation state of the elements on the surface. The additives mainly affect the number of Lewis acid sites, whereas the Brønsted acidity changes insignificantly. An analysis of the acidity data for the modified catalysts together with the electronegativities of the introduced elements revealed no regular relationship between these quantities.

The relationships established for the acid properties of the catalysts allowed us to compare these data with the parameters of these catalysts in *n*-pentane oxidation and to verify our assumptions as to the way the product selectivity varies. As follows from the data presented in Fig. 9, the citraconic anhydride selectivity increases with an increasing number of acid sites on the catalyst surface. This is consistent with the view that the probability of isomerization and, accordingly, the probability of the oxidation of the resulting isoparaffin into methylmaleic (citraconic) anhydride increase with increasing catalyst acidity.

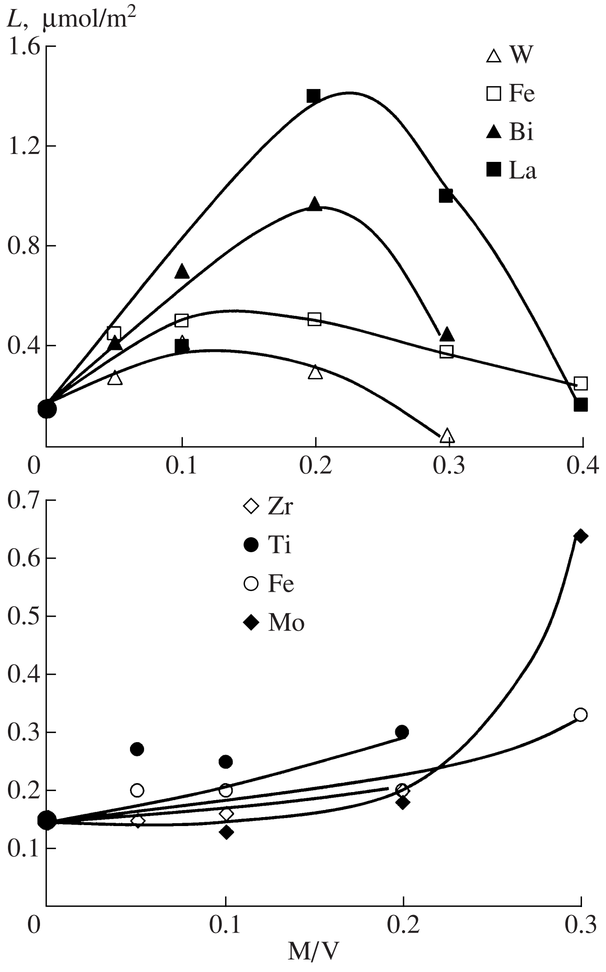

Fig. 8. Dependence of the amount of Lewis acid sites (*L*) on the additive content of the catalyst.

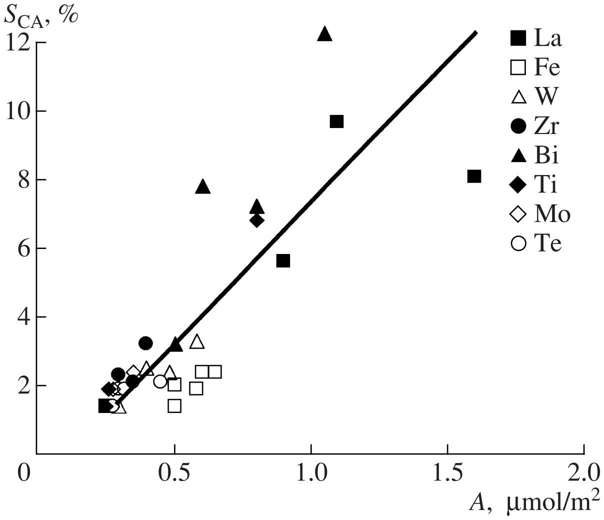

Fig. 9. Dependence of the citraconic anhydride selectivity on the number of acid sites in the VPMO catalysts.

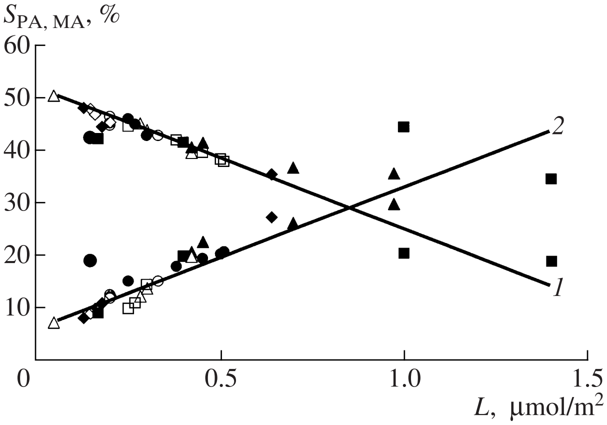

Fig. 10. Plots of the (*1*) maleic and (*2*) phthalic anhydride selectivities versus the number of Lewis acid sites for the VPMO catalysts.

On the other hand, our assumptions concern the influence of the acidity of the catalyst surface on the maleic and phthalic anhydride selectivity. An increase in the Lewis acidity should stabilize the olefinic and diolefinic structures involved in phthalic anhydride formation via the Diels–Alder reaction on the Lewis sites and should enhance the selectivity of the process with respect to this product. Accordingly, the maleic anhydride selectivity should decrease. In Fig. 10, the phthalic and maleic anhydride selectivity data for all of the catalysts are plotted against the surface concentration of Lewis acid sites. As can be seen from these data, the phthalic anhydride selectivity increases with an increase in the concentration of Lewis acid sites. This is in full agreement with our assumptions. The maleic anhydride selectivity decreases with an increase in the Lewis acidity.

Thus, we have verified the reaction mechanism–based assumption that the selectivity of *n*-pentane oxidation on VPO catalysts with respect to partial oxidation products can be controlled by modifying the acid properties of the catalyst. This opens up the way for further purposeful modification of the VPO catalysts in order to enhance their selectivity with respect to the partial *n*-pentane oxidation products.

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