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Methylpyrazine Ammoxidation over Binary Oxide Systems: V. Effect of Phosphorus Additives on the Physicochemical and Catalytic Properties of a Vanadium–Titanium Catalyst in Methylpyrazine Ammoxidation

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Abstract—Oxide vanadium–titanium catalysts modified by phosphorus additives ($20V_2O_5$–$(80 - n)TiO_2$–nP_2O_5, n = 1, 3, 5, 10, and 15 wt %) are studied in methylpyrazine ammoxidation. Two regions of compositions are found corresponding to radically different catalytic properties, namely, catalysts with a low (≤5 wt % P_2O_5) and high (≥10 wt % P_2O_5) concentration of the additive. In the first case, the introduction of phosphorus is accompanied by a gradual increase in the activity. In the second case, an increase in the additive concentration results in a decrease in the activity and selectivity to the target product, pyrazineamide, and a simultaneous increase in the selectivities to by-products, pyrazine and carbon oxides. The catalysts are characterized by X-ray diffraction analysis, differential dissolution, IR, and NMR spectroscopic data. As in the binary system, the active sites of the samples with a low concentration of phosphorus contain V^{5+} cations in a strongly distorted octahedral oxygen environment, which are strongly bound to a support due to the formation of V–O–Ti bonds. The catalytic properties of the samples containing ≥10 wt % P_2O_5 are due to the presence of the phase of a triple V–P–Ti compound with an atomic ratio V : P : Ti approximately equal to 1 : 1 : 1. The V^{5+} cations in this compound occur in a weakly distorted tetrahedral oxygen environment and are bound to the tetrahedral P^{5+} cations.

INTRODUCTION

Binary and modified vanadium–titanium catalysts are highly efficient in a number of reactions of selective oxidation and ammoxidation of aromatic [1, 2] and heteroaromatic [2] compounds, as well as in the selective reduction of nitrogen oxides with ammonia [3].

In our previous work [4], we have studied the effect of sodium and potassium additives on the physicochemical and catalytic properties of vanadium–titanium catalysts in methylpyrazine ammoxidation.

In this work we studied phosphorus-modified vanadium–titanium catalysts.

Previously reported data [5–12] on the modification of vanadium–titanium samples with phosphorus are rather scarce. Monolayer and submonolayer catalysts have received the most attention. The phosphorus concentration in the samples was varied over a wide range of P/V ratios, for example, from 0.25 to 5 in [5] and from 1 to 2 in [6].

There is no unified viewpoint in the literature on the nature of the interaction between the components in the modified samples and on the phosphorus effect on the structure of vanadium sites. Bond and Tahir [7] suggest that up to a P/V ratio of 1.5 : 1, phosphorus is present in the form of phosphate ions that are highly dispersed on the surface, which do not distort the structure of the active vanadium sites, the tetrahedral oxohydroxo complexes. Zhu *et al.* [5] believe that phosphorus first binds to vanadium to form the associates of the V–P–O compound at P/V > 1.25 that block the active sites, whereas at P/V = 5 the crystalline phases α-$VOPO_4$ and $(VO)_2P_2O_7$ are formed. Additionally, it has been shown in [8, 9] that phosphorus reacts with both vanadium and titanium to form phases of the corresponding phosphates, α- and β-$VOPO_4$ and β-$Ti(HPO_4)_2$. Deo and Wachs [10] emphasize that the effect of phosphorus is determined by both its concentration and the preparation procedure, particularly by the sequence in which vanadium and phosphorus are introduced, and propose a model for their interaction. It was found in [11] that the preliminary deposition of phosphorus on TiO_2 leads to the formation of the octahedrally coordinated vanadium sites.

The Lewis and Brønsted acidities of the P–V–Ti–O catalysts were measured by their activity in oxidative dehydrogenation and oxidative dehydration of isopropanol to acetone and propylene, respectively [7]. It was found that the addition of phosphorus is accompanied by an increase in the Brønsted acidity.

The catalytic properties of modified samples were studied in the oxidation of toluene [5, 12], *o*-xylene [12], butadiene [7], and methanol [10], as well as in the selective reduction of nitrogen oxides with ammonia [9]. In most reactions, an increase in the phosphorus concentration resulted in a decrease in the activity. Butadiene oxidation is an exception since the introduction of a considerable amount of phosphorus into the catalyst with P/V = 1.5 only slightly affected physicochemical and catalytic properties [7].

The authors of [5, 10] suggest that a decrease in the activity is due to a decrease in the number of active sites because of their blocking upon the interaction of vanadium with phosphorus. Along with the negative effect of phosphorus on the activity, the selectivity to the target product in the oxidation of *o*-xylene [12] and methanol [10] also decreases. The previously reported data on the effect of phosphorus on the selectivity in toluene oxidation are contradictory. It was found in [5] that with an increase in the P/V ratio, selectivity to the oxidation products of the CH_3 group decreases and selectivity to carbon oxides and the products of oxidative coupling increases. The authors propose a model of the P–V–O sites bound to the surface and the reaction mechanism. On the other hand, it was shown in [12] that a plot of the yield of benzoic acid vs. concentration of the phosphorus additive has an extremum and the maximum is observed at a ratio P/V of 1 : 1.4. The introduction of phosphorus results in a significant decrease in the initial selectivity to benzoic acid and the further oxidation of benzoic acid. The above changes are due to the influence of the additive on the surface acidity and to the differences in the acid–base properties of the initial compounds and reaction products.

Data on the catalytic properties of the P–V–Ti oxide catalysts in methylpyrazine ammoxidation are not available in the literature.

This work is aimed at the study of the effect of phosphorus on the physicochemical and catalytic properties of vanadium–titanium catalysts in methylpyrazine ammoxidation.

EXPERIMENTAL

The vanadium–titanium catalysts of the $20V_2O_5$–$(80 - n)TiO_2$–nP_2O_5 composition, n = 1, 3, 5, 10, and 15 wt %, modified with phosphorus, were studied.

Samples were prepared by mixing aqueous solutions of vanadyl oxalate and orthophosphoric acid with anatase followed by spraying the suspension, drying, and calcination in air at 450°C.

The specific surface area was measured by argon thermal adsorption [13].

The catalytic properties of the samples were studied in a flow setup with a GC analysis of the components of the reaction mixture [14]. Experiments were carried out in the temperature range 250–360°C with the reaction mixture having the following composition, vol %: methylpyrazine : oxygen : ammonia : steam = 1 : 8 : 17 : 17, and balance nitrogen. The fraction of 0.25–1 mm was used.

X-Ray diffraction analysis was performed on an URD-6 diffractometer (Germany) with filtered CuK_α radiation.

The IR spectra of the samples were recorded on a BOMEM-MB-102 spectrometer, and the weighed portion (2 mg) of the sample was pelleted with KBr.

The NMR spectra were recorded on BRUCKER MSL-400 and CXP-300 instruments at frequencies of 105.20 and 78.86 MHz (^{51}V) and 161.9 and 121.4 MHz (^{31}P), respectively. The chemical shifts ^{51}V and ^{31}P were measured relatively to $VOCl_3$ and 85% H_3PO_4. A detailed description of the procedure of the NMR study is presented in [15].

Chemical compositions of substances formed in the system were also determined by the method of differential dissolution (DD) [16] with the use of an atomic-emission spectrometer with inductively bound plasma.

RESULTS AND DISCUSSION

Figure 1 presents the diffraction patterns of the modified vanadium–titanium samples with different concentrations of additives. The binary catalyst contains a mixture of individual vanadia (V_2O_5) and anatase titania (TiO_2) with a small admixture of rutile. The introduction of a small amount of phosphorus (1 wt % P_2O_5) does not change the diffraction pattern and hence the phase composition of the sample. An increase in the additive concentration to 3 wt % results in the appearance of new reflections with d/n = 4.08, 3.66, 3.33, and 2.89 Å. The intensity of these reflections increases monotonically with a further increase in the P_2O_5 concentration, and low-intensity lines with d/n = 2.053, 1.797, and 1.576 Å additionally appear on the diffraction patterns of the samples with 10 and 15 wt % P_2O_5. Simultaneously, the intensities of the reflections typical of vanadium pentoxide gradually decrease until their complete disappearance in the sample of $20V_2O_5$–$65TiO_2$–$15P_2O_5$ wt % composition. The synchronism in the changes of the intensities of the new reflections and the phosphorus content can be evidence that they belong to the same individual compound. An attempt to identify it on the basis of the ASTM files showed that it was none of the known V–P–O, Ti–P–O, or V–Ti–O compounds.

When unknown compounds are formed and when it is necessary to determine their chemical composition, the method of differential dissolution [16] is rather efficient. Analysis of the kinetic curves of element dissolution and the stoichiograms (curves of a change in the ratio between different elements) allow one to estimate the qualitative chemical composition and fragmentary (without oxygen) formulas of the solid phases, as well as to simultaneously obtain data on their quantitative concentrations in the sample under study.

The determination of the composition of an unknown phase is based on the fact that during dissolution of the individual compound the ratios of its elements in a solution remain constant and coincide with the stoichiometric ratio of these elements in the solid.

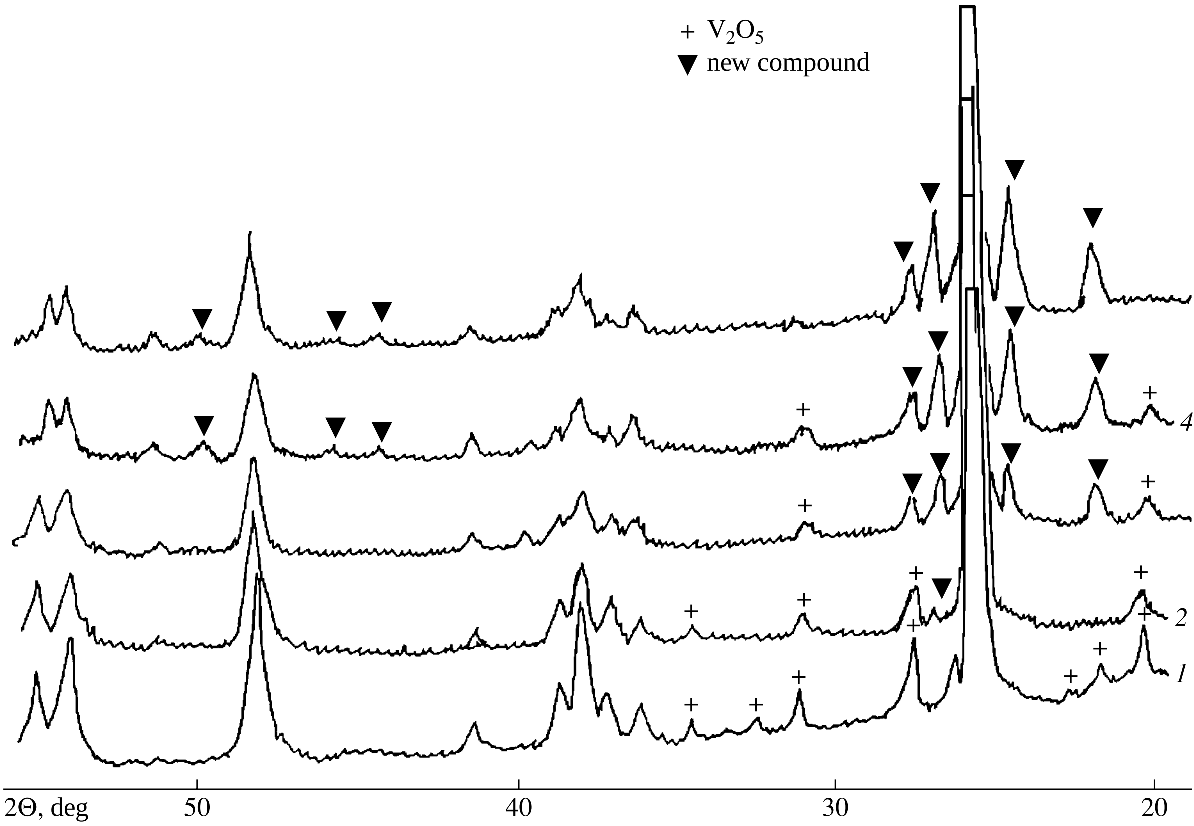


Fig. 1. Diffraction patterns of the modified samples containing (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 10, and (*5*) 15 wt P_2O_5.

Figure 2 shows the kinetic curves of dissolution of the catalyst elements and the corresponding stoichiograms (*S*) for the sample containing 10 wt % P_2O_5.

Vanadium transfer into the liquid phase occurs continuously during the whole period of the sample dissolution. Titanium and phosphorus pass into the solution after replacement of water as a solvent first by nitric acid (2 M) and then hydrofluoric acids (3.8 M). The main fraction of phosphorus dissolves in HNO_3 and that of titanium dissolves in HF.

At the beginning of dissolution in water, only a small amount of vanadium is present in the liquid phase, and this amount increases somewhat when nitric acid is used as a solvent and especially sharply on going to a stronger solvent (HF). Under these conditions, phosphorus and titanium also begin to pass into the solution. The concentration of the dissolved elements passes through a maximum with increasing duration and temperature of dissolution. The stoichiograms V/Ti, V/P, and Ti/P remain practically unchanged, indicating the dissolution of the individual compound containing phosphorus, vanadium, and titanium. The ratios between the elements in this compound are close; that is, V/P/Ti ≈ 1 : 1 : 1. With a further increase in the temperature and duration of dissolution, the concentration of dissolved titanium substantially increases. At the same time, the amounts of vanadium and phosphorus in the solution decrease. Note that in this case the concentrations of phosphorus and vanadium in the solution are also close.

It follows from the above findings that the samples contain three phases, which are different in the solubility and relative concentrations of components. The first phase that rapidly dissolves in water and diluted nitric acid represents an individual vanadium compound. The second phase that also dissolves rapidly in hydrofluoric acid is an individual compound with the ratio V/P/Ti ≈ 1 : 1 : 1. Note that the predominant fraction of vanadium and phosphorus in the sample containing 10 wt % P_2O_5 is present in this compound. The third phase dissolves in hydrofluoric acid at a temperature above 50°C and contains mainly titanium and slight admixtures of vanadium and phosphorus.

Taking into account XRD data, the first phase can be treated as vanadium oxide (V_2O_5) and the last phase as titanium dioxide. Hence, the second phase corresponds to an unidentified compound with an unknown structure. This compound contains phosphorus, vanadium, and titanium with a ratio of components close to unity and is characterized by the following set of the reflections in the diffraction pattern: $d/n = 4.08_7, 3.66_x, 3.33_8, 2.89_4, 2.053_1, 1.797_1$, and 1.576_1 Å.

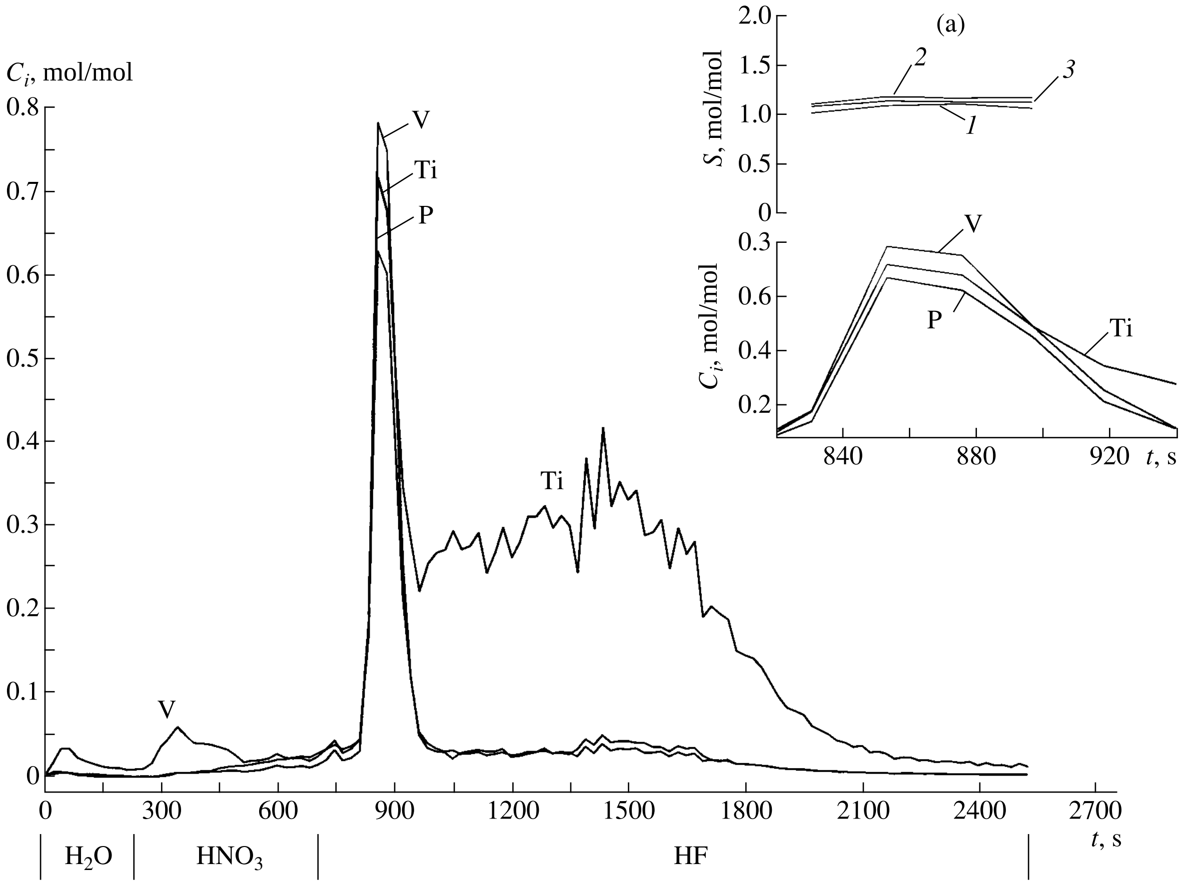


Fig. 2. Curves of dissolution of elements entering the sample with 10 wt % P_2O_5 vs. time of dissolution. (a) curves of dissolution and stoichiograms for (*1*) V/Ti, (*2*) V/P, and (*3*) Ti/P.

The curves of element dissolution can be transformed into the kinetic curves of dissolution of individual phases by stoichiographic calculations. Figure 3 presents an example of such a transformation for the sample containing 10 wt % P_2O_5. The simultaneous dissolution of the phase of the triple V–P–Ti compound and TiO_2 can indicate the strong binding of this compound to the surface of the highly dispersed anatase particles or the occurrence of this compound in the deep pores of TiO_2.

To obtain additional data on the new compound, the catalysts were studied by IR and NMR spectroscopy.

Figure 4 shows the IR spectra of the modified samples. When phosphorus is introduced (3 wt % P_2O_5), a broad absorption band in the region of 1050 cm^{-1} appears along with the absorption bands at 1023 and 933 cm^{-1} due to the vibrations of the V=O and V–O–V bonds in V_2O_5 typical of the binary sample and the intense absorption bands at 550 and 345 cm^{-1} due to TiO_2 (anatase) [17]. When the additive concentration increases, a series of new absorption bands appear in the regions of 1000–1200, 750–900, and 650–450 cm^{-1}. As in the case of XRD analysis, the spectra observed cannot be identified on the basis of the spectroscopic data available in the database for known compounds containing phosphorus, vanadium, titanium, and oxygen. Thus, one can conclude that the spectra belongs to a new V–P–Ti compound. Along with the appearance of the above absorption bands in the spectra of the samples with a high phosphorus concentration, the absorption band at 933 cm^{-1} (ν(V–O–V)) disappears and the absorption band at 1023 cm^{-1} (ν(V=O)) shifts to 1020 cm^{-1}, and its intensity monotonically increases. According to the XRD data, the amount of the V_2O_5 phase decreases with increasing phosphorus concentration. Hence, the absorption band at 1020 cm^{-1} can also be attributed to the triple compound. The absorption bands at 1165, 1098, 1020, and 1050 cm^{-1}, as well as those at 650, 590, and 471 cm^{-1} are typical of the stretching and bending vibrations, respectively, of the tetrahedral phosphate group PO_4^{3-} [18]. The absorption bands in the region 740–840 cm^{-1} are due to the stretching vibration of VO_4^{3-} ions in sodium orthovanadate Na_3VO_4 [19]. The absorption bands at 785 and 870 cm^{-1} found in the spectra of the modified samples are likely to

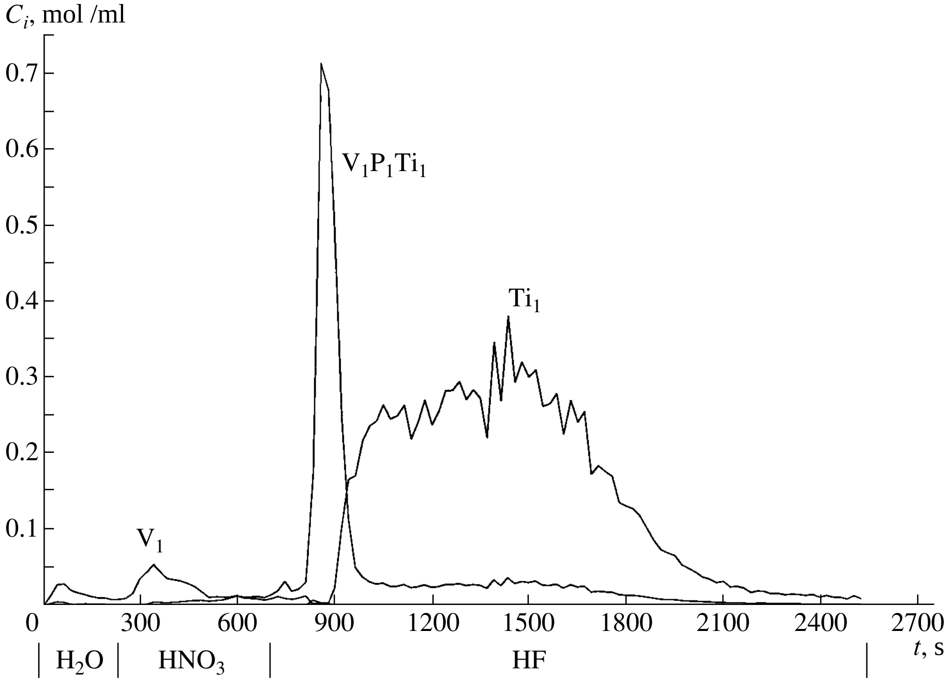


Fig. 3. Kinetic curves of dissolution of the individual compounds in the sample containing 10 wt % P_2O_5.

give evidence of the presence of V^{5+} cations in the tetrahedral oxygen environment in the V–P–Ti compound.

The NMR spectroscopy on the corresponding nuclei is the most informative method for the characterization of the local surrounding of cations.

Figure 5a presents the ^{51}V NMR spectra, and Fig. 5b shows the ^{51}V MAS NMR spectra of the samples modified by phosphorus additives. The spectra are the superposition of two lines. The first line with the axial anisotropy of the chemical shielding tensor and the parameters $\sigma_1 = \sigma_2 = -310$ ppm and $\sigma_3 = -1270$ ppm (Fig. 5a) has a well-resolved MAS spectrum (Fig. 5b). The second line with a maximum at –800 ppm (Fig. 5a) is not narrowed during sample spinning (Fig. 5b). The relative intensities of these lines depend on the amount of introduced phosphorus. At a low additive concentration (up to 5 wt % P_2O_5), the line with the axial anisotropy of the chemical shielding tensor prevails, while at a high additive concentration (≥10 wt % P_2O_5), the line with a maximum at –800 ppm prevails. The isotropic shift (–612 ppm), the anisotropy, and the parameters of the quadrupole tensor for the first line correspond to those for individual vanadium oxide V_2O_5 [20] in which V^{5+} cations are in the distorted octahedral oxygen environment. Taking into account XRD and differential dissolution data, the second line can be attributed to vanadium in the phase of the triple V–P–Ti compound. A small value of the chemical shielding anisotropy for this line indicates the weakly distorted tetrahedral coordination of V^{5+} cations, whereas a high value of the isotropic shift (800 ppm) points to their binding to phosphorus atoms through oxygen.

It has been shown previously [21] that two vanadium species, free (in the form of V_2O_5) and strongly bound to TiO_2, exist in the binary vanadium–titanium catalysts. The structure of the local environment of the second species was clearly recognized only after the removal of the vanadium pentoxide phase by washing with a HNO_3 solution according to a procedure described in [21]. The strongly bound vanadium occurs in the strongly distorted octahedral oxygen environment, and the constant of quadrupole coupling in its NMR spectrum is abnormally high, up to 15 MHz. Figure 5c presents the ^{51}V MAS NMR spectra of the modified samples washed with a solution of HNO_3. The spectra of the samples containing 1 and 3 wt % P_2O_5 are close to that of the binary sample [21] and also have a high constant of quadrupole coupling, indicating the presence of vanadium strongly bound to titanium. The spectrum of the sample containing 15 wt % P_2O_5 differs substantially from that of the binary catalyst and coincides with the spectrum of the unwashed sample of the same composition. This fact indicates that practically all of the vanadium occurs in the triple compound in which vanadium atoms are bound to the phosphorus atoms. Data obtained agree well with the findings of differential dissolution according to which the triple compound dissolves with a noticeable rate only in hydrofluoric acid. Thus, our data suggest that the introduction of phosphorus into the binary catalyst results in a gradual decrease in the amounts of both free vanadium and vanadium strongly bound to titanium and in the formation of the phase of the triple compound.

Figure 6a shows the ^{31}P MAS NMR spectra of the modified catalysts and the sample of titanium phosphate prepared by mixing an aqueous H_3PO_4 solution with anatase followed by drying and calcination in air at 450°C. The spectra of the modified samples represent a single line with a maximum at –30 ppm. This spectrum dramatically differs from that of titanium phosphate indicating the absence of the latter in the phosphorus-modified samples. A detailed analysis of the ^{31}P MAS NMR and ^{31}P spin echo spectra of the modified samples and various modifications of $VOPO_4$ (α_I-, α_{II}-, β-, δ-, and γ-), as well as their hydrated species [15], allowed us to reach a conclusion on the binding of phosphorus with V^{5+} cations through the oxygen atoms. None of the above vanadium phosphate phases are formed in the modified catalysts. An upfield shift of the ^{31}P line relative to the position in the spectrum of $VOPO_4$ suggests that phosphorus is bound to both vanadium and titanium.

Figure 6b presents the ^{31}P MAS NMR spectra of the modified samples washed with a solution of nitric acid. The spectrum of the sample containing 1 wt % P_2O_5 is a poorly-resolved line with a maximum around 0 ppm typical of vanadium phosphate. When the amount of P_2O_5 increases to 3 wt %, a narrow line at –30 ppm appears at the background of this signal (such a line was observed in the spectra of the unwashed samples), and its intensity increases significantly with a further increase in the phosphorus concentration. One can assume that phosphorus first reacts with V^{5+} cations only and then binds to titanium to form the triple V–P–Ti compound. To disclose the structure of this compound, we used the 2D 3QMAS and 5QMAS NMR methods [15], which allow one to obtain well-resolved spectra and to determine the distribution of parameters of the chemical shift and quadrupole tensors. According to the data of [15], the vanadium sites of only one type, V^{5+} in the weakly distorted tetrahedral oxygen environment, are formed in the triple compound. At the same time, significant deviations (different for each site) are observed in the second coordination sphere and this fact can be due to a structural disorder of this compound.

Hence, it follows from the data obtained that phosphorus interacts with both vanadium and titanium in the modified samples to form the triple compound with the ratio V/P/Ti ≈ 1 : 1 : 1 in which the vanadium(5+) and phosphorus(5+) cations occur in the weakly distorted tetrahedral oxygen environment. With an increase in the phosphorus concentration, the amount of this phase continuously increases and the amounts of the individual vanadium oxide and vanadium strongly bound to TiO_2 decrease, whereas the structure of the latter, a strongly distorted octahedron, does not change.

The catalytic properties of the binary and modified samples are presented in the table and in Fig. 7.

Methylpyrazine conversion to the reaction products over the binary vanadium–titanium catalysts is described by the following consecutive-parallel scheme [20]:

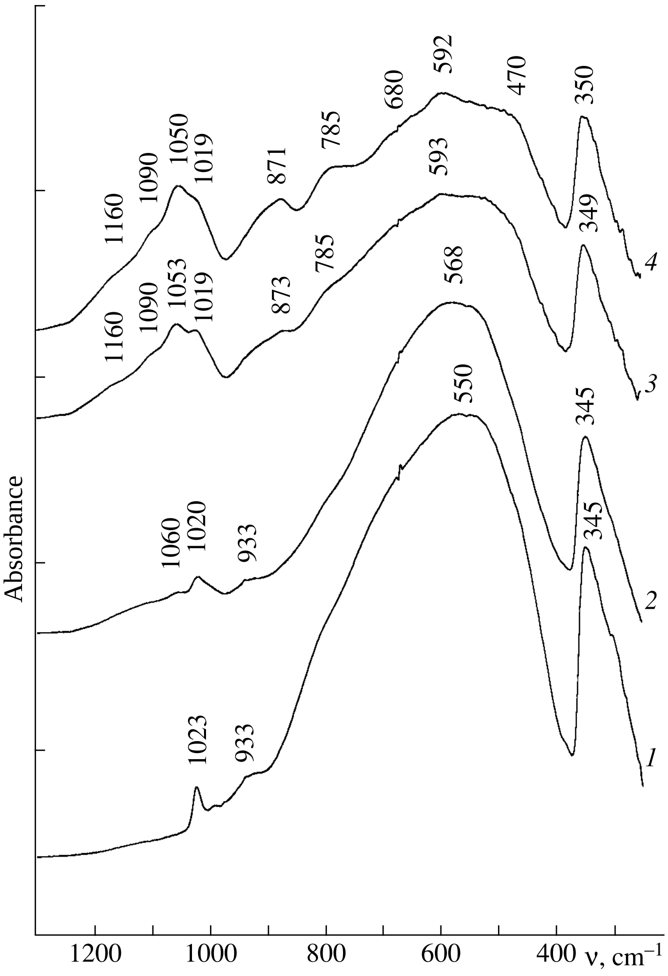
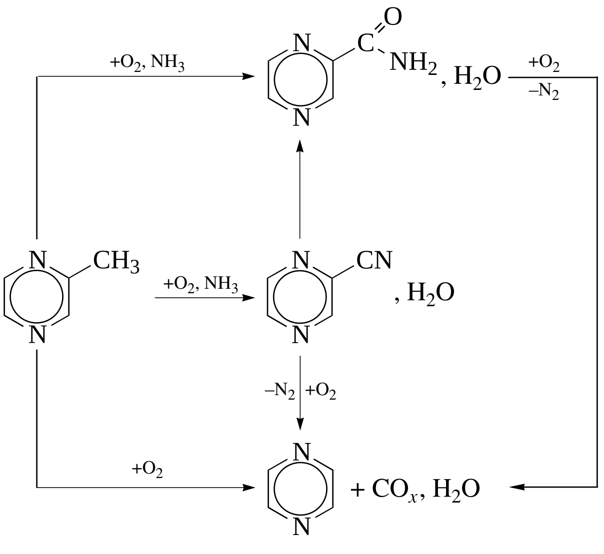


Fig. 4. IR spectra of the modified samples containing (*1*) 0, (*2*) 1, (*3*) 5, and (*4*) 15 wt % P_2O_5.



The main selective product is pyrazineamide (PA) formed both from methylpyrazine directly and from the

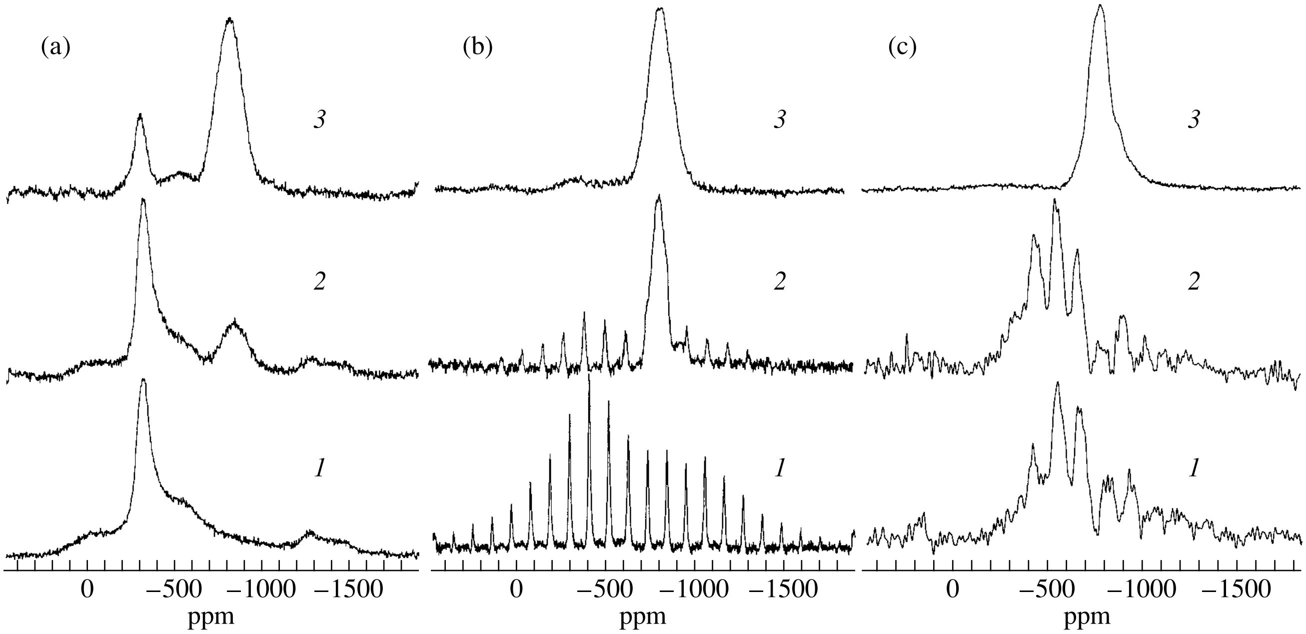


Fig. 5. (a) ^{51}V NMR spectra and (b) ^{51}V MAS NMR spectra of the modified samples containing (*1*) 1, (*2*) 5, and (*3*) 15 wt % P_2O_5 and (c) ^{51}V MAS NMR spectra of the samples containing (*1*) 1, (*2*) 3, and (*3*) 15 wt % P_2O_5 washed with HNO_3.

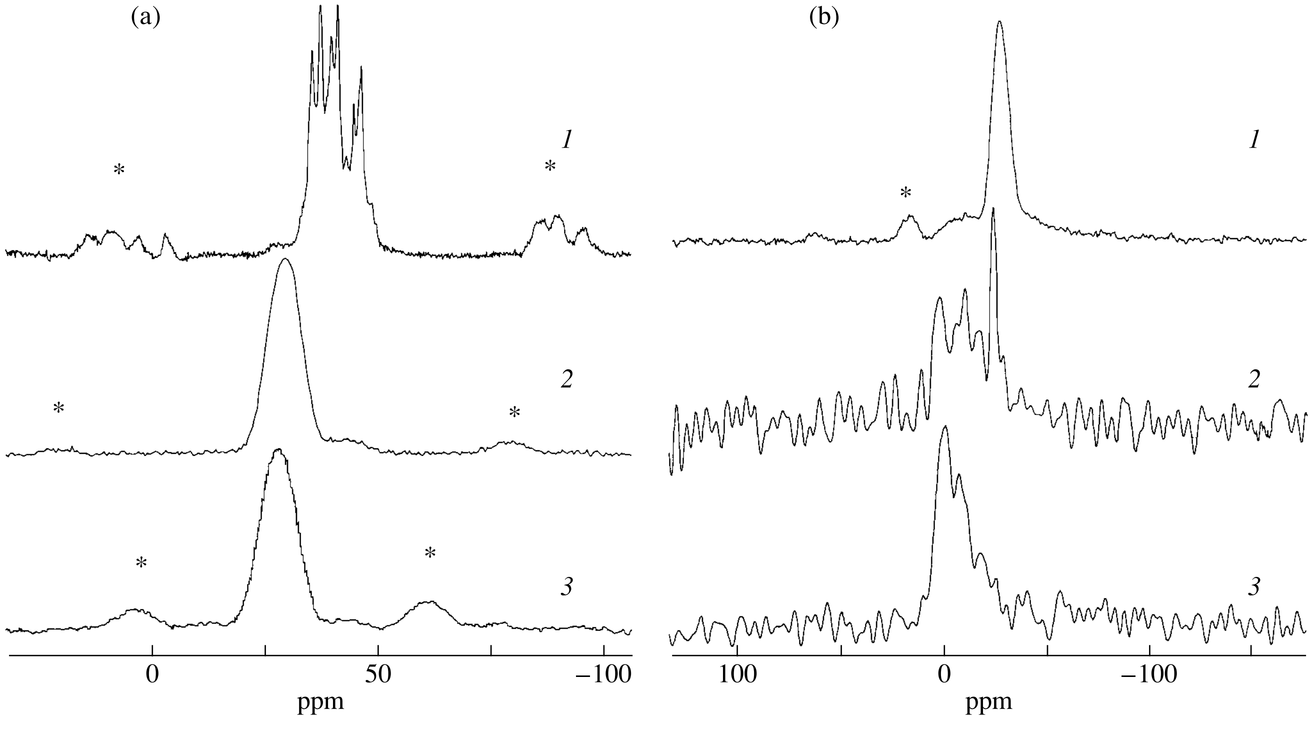


Fig. 6. ^{31}P MAS NMR spectra of (a) the modified samples containing (*1*) 3 and (*2*) 10 wt % P_2O_5 and (*3*) titanium phosphate; (b) the samples containing (*1*) 1, (*2*) 3, and (*3*) 10 wt % P_2O_5 washed with HNO_3.

Catalytic properties of the binary and phosphorus-modified vanadium–titanium catalysts in methylpyrazine ammoxidation. The contact time is 1.5 s

Concentration of P_2O_5, wt %	S_{sp}, m^2/g	T, °C	X, %	$k_{sp} \times 10^{-18}$, molecule m^{-2} s^{-1}	CO_x	Selectivity, %		
						P	PN	PA
0	27	250	33.5	0.45	1.6	5.9	11.8	80.1
		270	47.7	0.71	1.7	7.3	13.3	78.0
		300	74.7	1.53	4.0	16.7	22.3	56.7
		320	90.4	2.79	8.1	32.0	20.4	39.4
1	26	250	32.3	0.44	1.4	5.6	12.4	80.6
		270	52.1	0.73	1.6	6.8	13.3	78.3
		300	77.0	1.76	5.1	16.5	16.0	62.4
		320	88.2	2.64	11.8	32.1	12.2	44.4
3	24	250	31.3	0.51	1.3	5.3	12.0	81.4
		270	51.3	0.76	1.5	6.7	13.5	78.3
		300	75.9	1.72	5.0	16.0	15.0	64.0
		320	89.3	3.21	12.0	33.7	11.0	44.7
5	19	250	33.4	0.64	1.3	5.2	11.5	82.0
		270	49.1	0.99	1.6	7.2	13.4	77.8
		300	76.7	2.11	5.2	17.0	11.7	66.2
		320	88.5	3.66	13.5	32.9	11.1	44.4
10	17	270	25.8	0.41	8.7	23.2	13.3	55.3
		300	37.8	0.79	11.2	34.3	17.2	37.3
		360	79.4	2.38	27.1	31.5	17.1	20.3
15	15	270	22.2	0.40	7.5	22.2	13.0	57.3
		300	33.4	0.73	10.3	33.4	18.5	36.6
		360	70.2	1.79	23.8	34.8	20.6	20.8

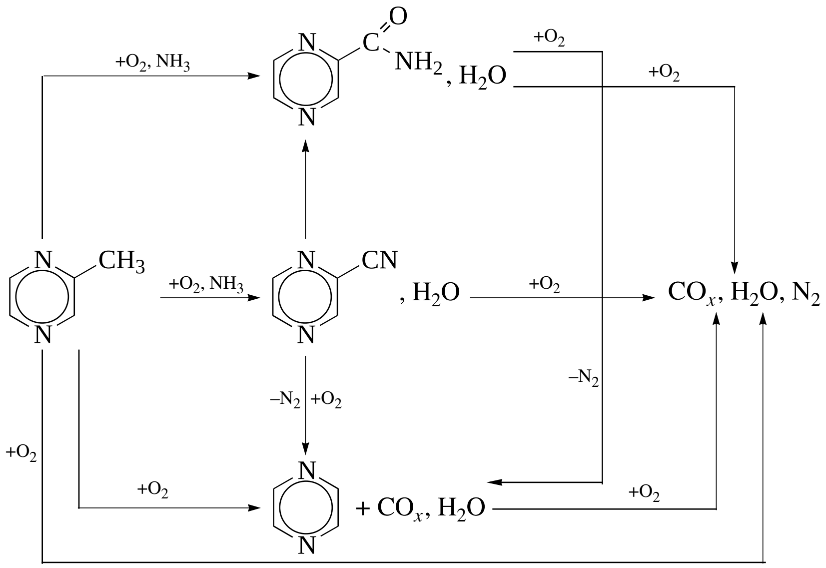
second selective product, pyrazonitrile (PN), through the consecutive route of high-temperature hydrolysis. The ratio of selectivities to the by-products, pyrazine (P) and carbon oxides (CO_x), is close to 4, and this is due to the oxidative dealkylation of methylpyrazine and its derivatives (PA + PN) without destruction of the heteroaromatic ring, as followed from the analysis performed by us in [13].

When phosphorus was introduced, the same products are formed but the selectivities to reaction products and the activity of the samples change.

One can separate two regions of compositions with low (≤5 wt % P_2O_5) and high (≥10 wt % P_2O_5) additive concentrations, which differ significantly in their performance. In the first case, the introduction of phosphorus is accompanied by a gradual increase in the activity. In the second case, the activity drops with an increase in the additive concentration and, as a result, the comparable methylpyrazine conversions are reached at a higher reaction temperature.

Figure 7 shows selectivities to the reaction products at a methylpyrazine conversion of 35 ± 2% vs. the phosphorus concentration in the samples.

As can be seen from Fig. 7, when the additive concentration is up to 5 wt % P_2O_5, the selectivities to all the reaction products remain unchanged. On going to the samples with high phosphorus concentrations, the selectivities change substantially. The selectivity to amide decreases and those to pyrazine and carbon oxides increase, whereas the selectivity to nitrile is close to that over the binary catalyst. At a high methylpyrazine conversion, the variations of selectivities are more pronounced. The low ratio of the selectivities to pyrazine and CO_x (<2.5) observed over these samples can point to the destruction of the heteroaromatic ring of both the initial compound and the heterocyclic reaction products. Hence, the introduction of $\geq$10 wt % P_2O_5 in the vanadium–titanium catalyst results in the appearance of additional routes for the formation of carbon oxides via the parallel and consecutive routes:



Note that over the samples with a low phosphorus concentration at high methylpyrazine conversions the selectivity to nitrile decreases and that to amide increases compared to the selectivities over the binary catalyst.

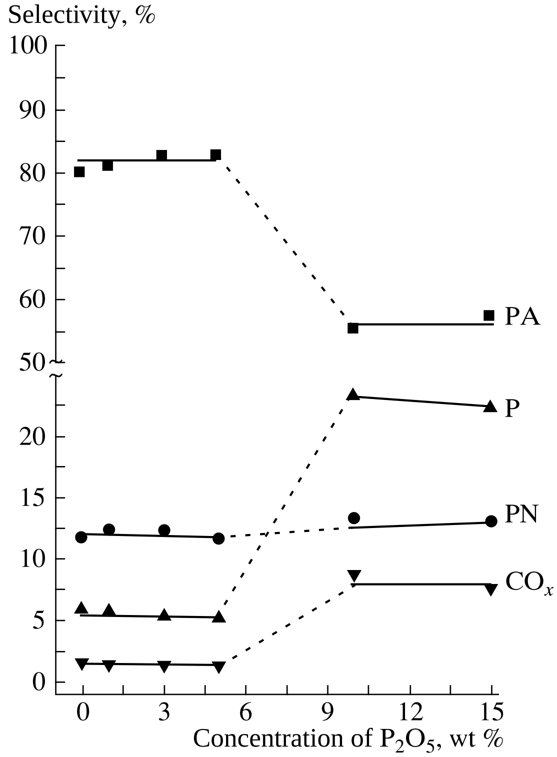


Fig. 7. Selectivities to the reaction products vs. the phosphorus percentage in the samples at a methylpyrazine conversion of 35 ± 2%; PA, pyrazineamide; P, pyrazine; and PN, cyanopyrazine.

Figure 8 shows the activation energy of the total methylpyrazine conversion vs. the phosphorus percentage.

It is also possible to separate samples with low and high contents of the additive by the degree of influence of phosphorus on the activation energy. In the first case, the introduction of phosphorus does not affect the activation energy. The constancy of the activation energy can indicate that the active sites do not change upon the introduction of phosphorus in this range of concentrations. An increase in the phosphorus concentration up to 10 wt % P_2O_5 leads to a stepwise change in the activation energy (from 10 to 18 kcal/mol). A further increase in the phosphorus concentration in the sample does not markedly affect the activation energy.

The following conclusions can be drawn from comparison of the catalytic and physicochemical characteristics. In the samples with a low phosphorus concentration as in the binary system, the active sites contain V^{5+} cations in the strongly distorted octahedral oxygen environment, which are strongly bound to the support due to the formation of the V–O–Ti bonds. The activity growth observed and the redistribution of selectivities can be due to a change in the acceptor properties of the vanadium sites upon the introduction of phosphorus as an acid additive. The strengthening of the acceptor properties can favor both higher coverage with the adsorbed species of the initial compound, which is a weak organic base, and stronger adsorption of the weakly basic reaction products. On the one hand, it can lead to an increase in activity and, on the other hand, to the destruction of the heterocycle. Since pyrazineamide is formed not only from methylpyrazine directly but also from pyrazinonitile via the consecutive route, one

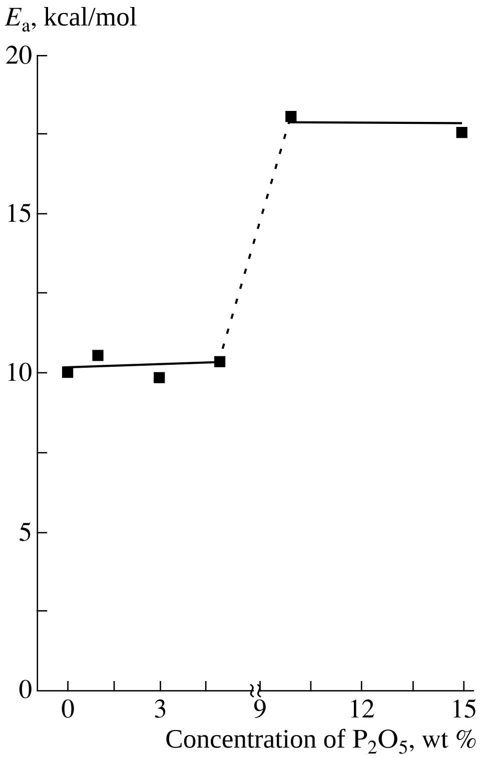


Fig. 8. (a) Activation energy of the total methylpyrazine conversion and (b) the specific activity at the reaction temperature 300°C vs. the phosphorus percentage in the samples.

can suggest that the introduction of phosphorus favors nitrile hydrolysis.

The catalytic properties of the samples containing ≥10 wt % P_2O_5 are determined by the presence of the phase of the triple V–P–Ti compound in which V^{5+} cations are in the tetrahedral oxygen environment and are bound to P^{5+} cations. These sites are less active and selective than V^{5+} in the distorted octahedral oxygen environment and are strongly bound to the support due to the formation of the V–O–Ti bonds.

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