

CHEMICAL TECHNOLOGY

UDC 661.725.3

<https://doi.org/10.31489/2021Ch2/53-62>

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Catalytic conversion of isopropyl alcohol on the heteropolic acid – titanium oxide system

A complex of modern physicochemical methods (X-ray phase analysis, low-temperature adsorption of nitrogen, scanning electron microscopy, element analysis) was used to study the phase and texture properties of the phosphomolybdenum heteropoly acid–titanium oxide catalytic system. It was found that the optimal content of phosphomolybdenum heteropoly acid, which leads to an increase in the catalytic activity of titanium dioxide, is 7% wt.: the diisopropyl ether yield is higher, it reaches maximum values in a shorter period of time, and the samples are characterized by greater stability. It is shown that the textural characteristics of the specific surface area and dispersion are not the key factors responsible for the catalytic activity. It has been suggested that the activity of phosphomolybdenum heteropoly acid-containing samples is associated with the emergence of a new type of active centers that exhibit increased electron-donor properties (terminal oxygen atoms of the outer fragments of octahedra $M = O$ heteropolyacids). A drop in the catalytic activity of samples with a phosphomolybdenum heteropoly acid content of more than 7% wt. associated with the formation of surface metaphosphoric acid and entails a decrease in active centers.

Keywords: isopropyl alcohol, titanium dioxide, phosphomolybdenum heteropoly acid, phase composition, morphology, catalysis, diisopropyl ether, texture analysis, metaphosphoric acid, metatitanic acid.

Introduction

The constant interest in heteropoly acids (HPA) on the part of researchers is due to their unique physicochemical and catalytic properties [1–4]. In catalysis HPA of the Keggin structure $HnXM_{12}O_{40}$ ($X = P^{5+}$ and Si^{4+} , $M = W^{6+}$ and Mo^{6+}) are most often used. The acidic properties of these HPA were studied quite deeply and in detail, which served as the basis for the creation of several industrial processes with their participation [5–7].

There are three ways to use HPA as catalysts: the use of acid solutions, the use of bulk acids and the use of HPA supported on various carriers. Among the latter, many porous materials are used (silica gel, activated carbon, alumina, etc.) [8–12].

In previously published works [13, 14], the results of catalytic conversions of isopropyl alcohol on the HPA – η -alumina system were discussed. It was found that the modification of HPA leads to an increase in the activity of η -alumina and selectivity for oxygen-containing products. Based on a comparative analysis of the reaction products, it was found that the active centers of unmodified η -alumina are exclusively Lewis centers: strong Lewis acid centers and strong Lewis basic centers, whereas after the modification of HPA they are mainly represented by Bronsted bases. The resulting systems were characterized by X-ray phase analysis, scanning electron microscopy, elemental analysis, and IR spectroscopy. The totality of the results made it possible to establish that during the interaction of the Keggin structure with the basic oxide its destruction occurs and the heteropolyanion is formed, which, having a negative charge, interacts with the electron-acceptor

Lewis acid centers on the surface, forming a surface complex of the surface-ligand type, which has uncompensated negative charge, and then begins to act as the new foundation of Bronsted.

Taking into account these results, as well as studies in which HPA, in particular tungstenosilic acid (HSiW), supported on TiO₂ and SiO₂ exhibits high activity and selectivity in the process of dimethyl ether formation [8, 14–18], it was of interest to continue this direction. The present work is devoted to the study of the features of the conversion of isopropyl alcohol to diisopropyl ether in the presence of phosphomolybdenum HPA applied to titanium dioxide.

Experimental

A catalyst of a given composition was prepared by impregnating titanium dioxide with a solution of HPA in an aqueous solution of ammonia (based on HPA per carrier) onto a carrier previously calcined for 3 hours to 200 °C. During the process, the following compounds were used:

- 1) industrial titanium dioxide TiO₂ (Evonik Resource Efficiency GmbH);
- 2) phosphorus-molybdenum heteropoly acid (GPC) H₇ [P (Mo₂O₇)₆]·H₂O;
- 3) isopropyl alcohol (GOST 9805-84).

The catalytic properties of the starting and modified TiO₂ were studied on a flow through setting in the temperature range of 150–250 °C with a bulk feed rate of 75 h⁻¹.

The analysis of raw materials and liquid reaction products was carried out by a chromatographic method on a CHROM 5 instrument with a flame ionization detector using a column filled with a sorbent — CELIT S-22, with 17 % polyethylene glycol applied to the sorbent. The reaction gas products were analyzed on a CHROM 5 chromatograph with a thermal conductivity detector. Diethylene glycol ether and n-butyric acid deposited on the Inzen brick INZ-600 were used as the sorbent. The quantitative interpretation of the chromatographic peaks included in the composition of the obtained catalysis was determined by the method of absolute calibration and internal normalization.

The phase analysis of the samples was studied by X-ray phase analysis on a RIGAKU SC-70 instrument in the range of angles of 3–60 °C at an angular scanning speed of 10 deg/min in CuK radiation (40 kV, 15 mA). The interpretation of the diffraction patterns was carried out using the ICDD database, PDF-2.

The surface morphology, as well as the elemental composition of the samples, was studied by scanning electron microscopy (SEM) on a JEOL JSM-6610 LV instrument with a 0.14 nm lattice resolution (with an integrated EDX analyzer (EDS, Genesis 4000, using Si(Li) detector) at an accelerating voltage of 100 kV. The SEM sample was mounted on carbon substrates mounted on copper grids. The statistical particle diameter was measured by SEM analysis of the sample.

The specific surface and pore volume were measured by adsorption–desorption of nitrogen on a universal analyzer ASAP 2400 (Micromeritics, USA). In the calculation the surface area of the nitrogen molecule was taken to be 0.162 nm², and the density of nitrogen in the normal liquid state was 0.808 g/cm³. The measurement accuracy was ±3 %. Adsorption isotherms were obtained at –196 °C after degassing of the sample at 500 °C to a residual pressure of 0.013 Pa. The pore volume and their diameter distribution were calculated based on the desorption branch of the isotherm using the standard Barrett-Joyner-Highland procedure (measurement accuracy ±13 %).

Results and Discussion

Catalytic properties

The catalytic activity and selectivity of the formation of isopropyl alcohol conversion products are shown in the Figure 1. It should be noted that the presented results were reproduced upon repeated preparation of samples of each composition. Over the entire temperature range studied the conversion of isopropyl alcohol increased the stronger, the higher the content of HPA was. The minimum conversion value was observed for a sample containing 5 % wt. HPA: it is 16.7 % at 150 °C and increases to 43.8 % at 250 °C (the latter value is almost identical to unmodified titanium dioxide). In the low-temperature region the highest conversion is typical for 13 % wt. of the sample, which reaches 54 %, significantly exceeding the others, but with rising in temperature to 250 °C the conversion of 7, 10, and 13 % of HPA-containing catalysts becomes almost the same (from 71 to 76 %).

The main products of the conversion of isopropyl alcohol under the reaction conditions were diisopropyl ether, propylene and water. In addition, in the presence of a 5 % HPA-containing sample at temperatures of 200 and 250 °C the formation of a small amount of acetone was noted. The highest ether selectivity was observed for 7 % and 10 % of HPA samples.

Table 1 presents the data on the selectivity and yield of ether depending on the composition of the catalyst obtained within 12 hours of the process (here it is necessary to clarify: the process was not carried out continuously, but for 3 intervals, when every 4 hours of “work” were followed by “rest” of the catalyst, after which the process was resumed again). As can be seen from the results presented in the table, the process of conversion of isopropyl alcohol in the presence of titanium dioxide modified with phosphoformolybdenum HPA differed in characteristic features. If the initial titanium dioxide had the highest ether yield every time after three hours of catalyst operation, after which a sharp drop was observed, the trend for the modified samples is different: the yield of ether in HPA-containing samples is higher (with the exception of 5% HPA), in addition, the catalyst went down these parameters after already 1 hour, and they remained stable until the end of the current interval. Here we are not faced with the task of finding an explanation for this fact, we only fixed the trend. In general, the 7% HPA + TiO₂ catalyst is most active: the diisopropyl ether yield from the 2nd to the 4th hour of each operation interval is 20.5–22% with an ether formation selectivity of 49.2–77.1%.

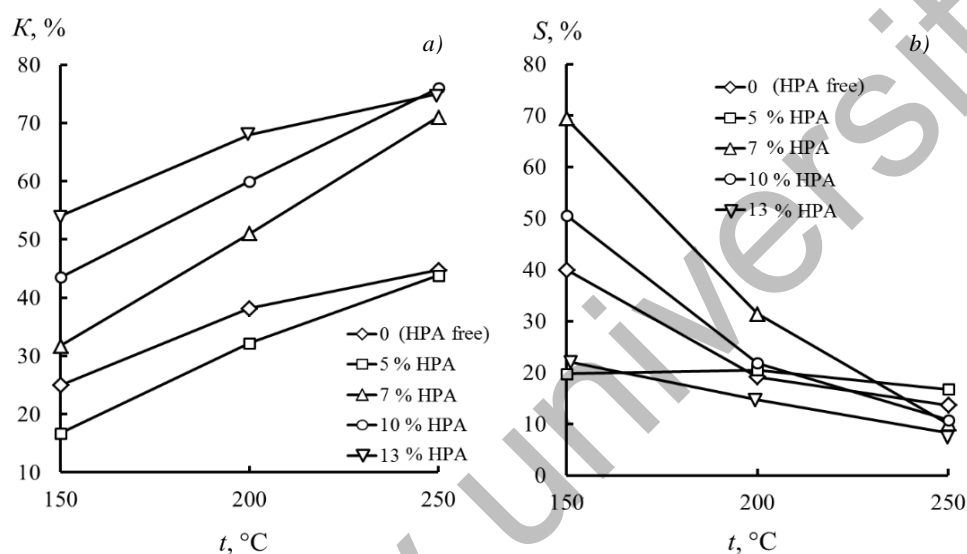


Figure 1. The effect of the composition of the catalyst on the conversion of (a) isopropyl alcohol and the selectivity (b) of the formation of diisopropyl ether

Table 1

Effect of duration on process indicators

Duration, hours	Composition of the catalyst									
	TiO ₂		5 % HPA + TiO ₂		7 % HPA + TiO ₂		10 % HPA + TiO ₂		13 % HPA + TiO ₂	
	S, %	α , %	S, %	α , %	S, %	α , %	S, %	α , %	S, %	α , %
1	46.7	4	9.6	1.6	28.8	6.7	18.3	6.5	30	12
2	30.9	6.7	15.2	3.3	66.2	21	50.6	22	28.9	13
3	40.1	10	16.4	3.4	69.4	22	40.5	21.9	23.9	12.9
4	60.2	8	16.5	3.3	77.1	21.6	37.1	22.1	41.0	13
5	40.2	8	8.5	1.7	52.2	16.7	32.3	16.4	39.5	15
6	37.6	8	12.3	2.7	56.7	21	35.4	18	30	18
7	26	9.2	12.9	2.7	55	20.9	41.4	18.2	30.5	18.3
8	22.9	6	10.5	2.1	55	20.2	45.2	18.1	41.6	18
9	11.6	3	5.2	1.3	42.9	16.3	29.5	15	33.7	14
10	16.6	4.8	7.4	2	50.1	20.9	27.1	16	23.8	15
11	18.6	5.2	7.2	1.2	49.2	20.8	30.0	16.1	23.9	15.1
12	13.9	1.6	6.4	1	56.7	20.8	32	16	44.1	15

Notes. The process temperature is 150 °C. Designations: S — selectivity, α — yield of diisopropyl ether.

Phase composition

Figure 2 shows the diffractograms of titanium dioxide before and after the introduction of HPA.

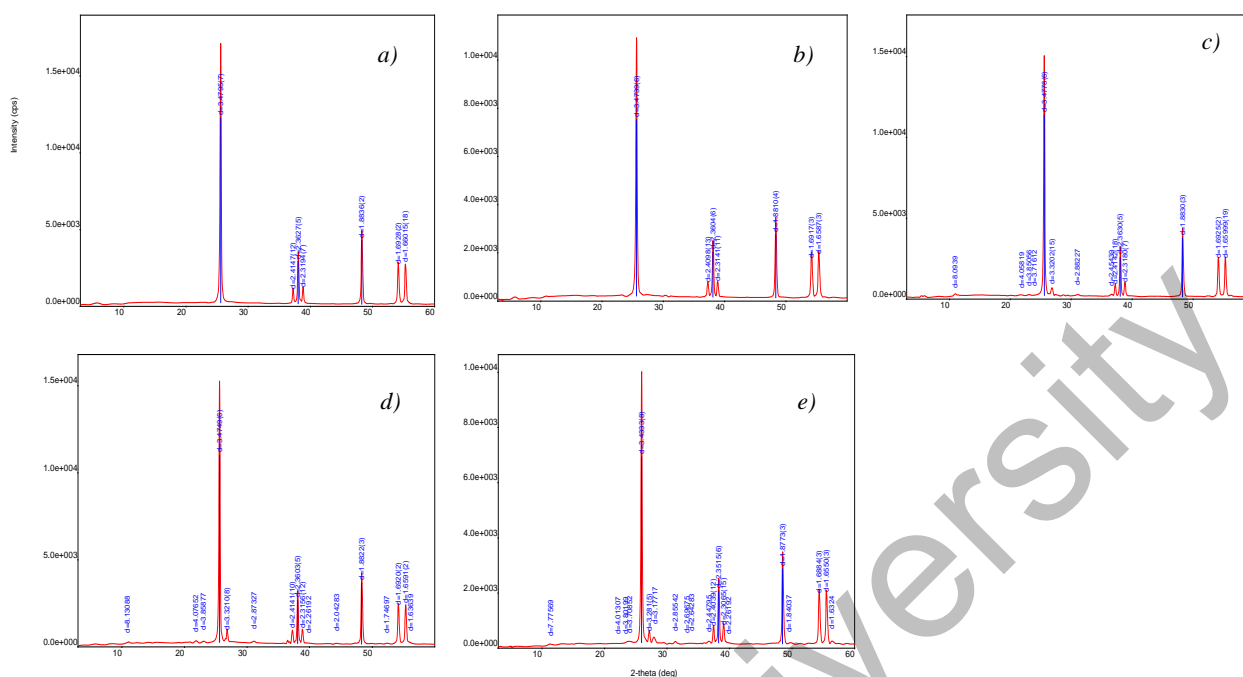


Figure 2. The diffractograms of titanium dioxide: the original, not containing HPA (a), containing 5 % wt. HPA (b), 7 % wt. (c), 10 % wt. (d) and 13 % wt. (e)

As can be seen from Figure 2a, the initial unmodified titanium dioxide is a well crystallized phase, anatase with characteristic narrow and high diffraction reflections at 25.58, 37.20, 38.06, 38.79, 48.28, 54.13 and 55.29 ° 2 θ (the interplanar distances of this phase are unchanged for all 5 samples). Type of diffraction pattern when entering 5 % wt. GPC (Fig. 2b), with the exception of a decrease in the intensity of all reflexes, does not change; the appearance of the HPA phase is not noted; the crystallinity of anatase is preserved. The decrease in the intensity of reflexes of the anatase phase here and hereafter is probably associated with the appearance of microstresses caused by the introduction of the modifier. With an increase in the content of HPA up to 7 % of the mass (Fig. 2c) along with the anatase present on the diffractogram, the appearance of new reflections corresponding to five new phases is noted: 56.32 ° 2 θ — TiMoO₄; 21.7, 36.56 and 44.39 ° 2 θ — H₂Ti₅O₁₁·H₂O; 10.89, 15.53 and 31.02 ° 2 θ — HPA (H₃PMo₁₂O₄₀·21H₂O); 26.86, and 52.37° 2 θ — H₃P₃O₁₀·2H₂O, as well as 32.01 and 47.04 ° 2 θ — PO₄, in addition, a decrease in the crystallinity of the sample was noted. The increase in the content of HPA to 10 % wt. (Fig. 2d) does not lead to a significant change in the phase composition relative to the previous sample, with the exception of the appearance of another phase of titanium dioxide — brookite (weakly intense reflections at 39.68 and 52.24 ° 2 θ). In the last of the studied, 13 % HPA-containing sample (Fig. 2e), of the previously marked six phases, there are reflexes related to only three phases, namely TiO₂ (anatase — 25.55, 37.17, 38.02, 38.73, 48.25, 52.24, 54.1, 55.26° 2 θ and brookite — 39.75° 2 θ), H₂Ti₅O₁₁·H₂O (7.98, 21.49, 36.19° 2 θ), H₃PMo₁₂O₄₀·21H₂O (10.92, 15.33, 18.46 and 31.02° 2 θ). In addition, this sample is also characterized by the greatest amorphism. Of undoubted interest is the fact that the PO₄ phase observed in the sample 7 % was not detected in subsequent samples.

Texture analysis

The textural characteristics and the content of elements in the samples are given in Table 2 and in the Fig. 3. The introduction of HPA leads to a decrease in the specific surface and pore volume by 15.8–35 % and 8.3–29.2 %, respectively, relative to unmodified titanium dioxide. The presence of HPA is also accompanied by a decrease in the total pore volume. It can be assumed that with a GPC content of up to 10 % wt. its compounds are located mainly in smaller pores (pores < 5 nm in size decrease up to 10 times compared to the initial titanium dioxide; Table 2), which leads to their “overgrowing”, while with an increase in the content of HPA over 10 % wt., — on the contrary, in a wide pore space.

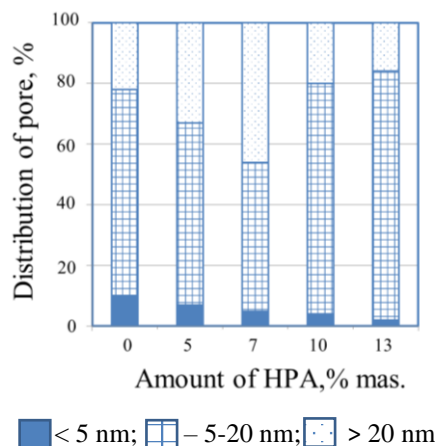


Figure 3. The effect of the amount of HPA on the distribution of pore volume by diameter:

Table 2

Physical-chemical characteristics of the samples

№ of the sample	HPA content, wt. %	S_{BET} , m^2/g	V_{pores} , cm^3/g	Phase composition (according to the results of X-ray phase analysis)	Elements content, mass. %		
					Ti	Mo	P
1	-	57	0.24	TiO ₂ (anatase)	59.04	-	-
2	5	31	0.21	TiO ₂ (anatase)	55.1	2.94	0.48
3	7	47	0.22	TiO ₂ (anatase), TiMoO ₄ , H ₂ O ₅ P ₁₁ ·H ₂ O, H ₃ PMo ₁₂ O ₄₀ ·21H ₂ O, H ₃ P ₃ O ₁₀ ·2H ₂ O, PO ₄	54.9	4.89	0.64
4	10	42	0.22	TiO ₂ (anatase, brookite), TiMoO ₄ , H ₂ O ₅ P ₁₁ ·H ₂ O, H ₃ PMo ₁₂ O ₄₀ ·21H ₂ O, H ₃ P ₃ O ₁₀ ·2H ₂ O, PO ₄	53.3	6.93	0.81
5	13	43	0.22	TiO ₂ (anatase), H ₃ PMo ₁₂ O ₄₀ ·21H ₂ O, iMoO ₄	47.3	10.06	0.97

Note. S_{BET} is the specific surface area by BET; was determined by single-point nitrogen adsorption at $p = 135$ Torr and $T = 77\text{K}$.

According to SEM data (Fig. 4), the surface of the initial titanium dioxide is represented by numerous isolated irregular crystallites, mainly 21–60 μm in size. In addition to isolated particles, a non-significant number of their aggregates with a size of 81–100 microns also can be seen. It should be noted that, without exception, all HPA-containing samples are characterized mainly by the content of crystallites of larger average sizes (41–80 μm) than the initial sample, which indicates a decrease in the dispersion of surface particles in the presence of HPA and is consistent with the above texture data analysis.

By means of an EDX analysis the spectra of the five test samples were obtained, which made it possible to reveal the peculiarities of the localization of phosphorus in a sample containing 13 % HPA. The distribution maps of titanium, molybdenum and phosphorus in this sample also confirmed the presence of a certain heterogeneity in the distribution of phosphorus.

Summarizing the study, we note that based on the nature of the modifier and the data obtained, it can be assumed that the increased selectivity for diisopropyl ether 7 % wt. HPA-containing titanium dioxide in the process of conversion of isopropyl alcohol is associated with the emergence of a new type of active sites, which exhibit enhanced electron-donor properties. Provided that the integrity of the HPA structure is preserved after its introduction into the composition of titanium dioxide (and this fact is confirmed by the data of phase analysis), the oxygen atoms included in the HPA can act as such centers. Taking into account that 12 terminal oxygen atoms of the outer fragments of the $M = O$ octahedra can act as electron donor centers in the structure of phosphomolybdic acid, the quantitative growth of the basic centers with the introduction of HPA is natural. It is likely that the aforementioned low activity of modified titanium dioxide in ether with an HPA content of up to 7 % is associated with an insufficient concentration of a new type of active sites. does not seem possible to it unambiguously explain the noted drop in catalytic activity when the content of HPA is higher than 7 % wt. The authors assume that the reason for these differences is the peculiarity of the distribution of phosphorus, or rather, a sharp increase in the content of metaphosphoric acid ($\text{H}_3\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$) due to the combination of surface tetraders of PO_4 into

rings. An indirect confirmation of the formation of metaphosphoric acid is the appearance of its additional reflex at 22.5 °C 2θ in 13 % of the HPA sample. Whether this is accompanied by an increase in the acidity of the catalyst, as stated in the work [19] is the subject of further research.

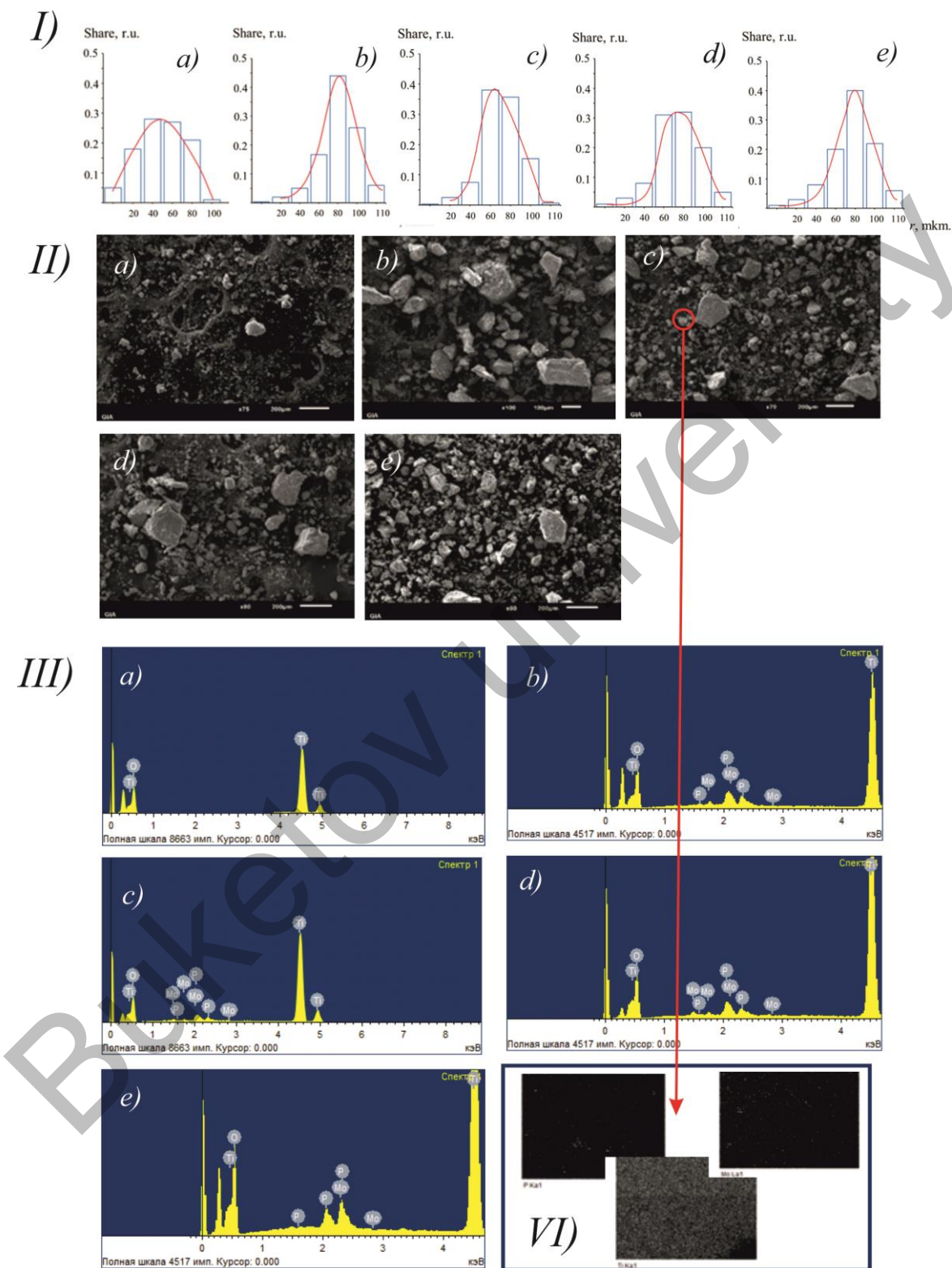
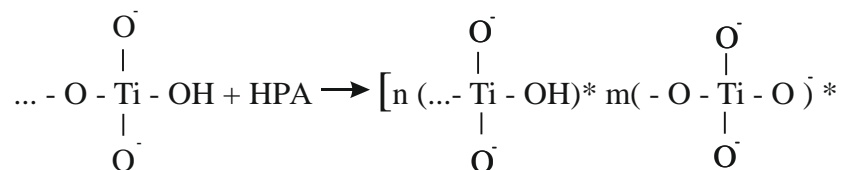


Figure 4. Comparative SEM-characteristic of titanium dioxide samples before (a) and after the introduction of HPA (b — 5 % by weight of HPA; c — 7 % by weight of HPA; d — 10 % by weight of HPA; e — 13 % by weight of HPA):

I — size distribution of crystallites; II — micrographs obtained by SEM; III — EDX spectra;

IV — Cards of elemental composition of 13 % GPC-sample

The formation of metacids can be explained as follows: it is the interaction of titanium dioxide with HPA can be represented as an acid-acid interaction, which leads to the formation of a surface polymer compound due to the complexation of two acids:



where * HPA, $\text{HPAn}^{x-} (m + 4k - y) \text{H} +]^{y-*} y \text{H}$, where $(\dots - \text{O}-\text{Ti}-\text{O}-)$ and HPAn^x- are heteropolyanions, which cause the charge of the polymer particle and stabilize its formation on surface.

In this case, according to the literature data [20–22] the acid–acid interaction is carried out due to the formation of hydrogen bonds between the hydrogen atoms of the carrier surface and the oxygen atoms in the HPA structure.

The fact of the discovery of such an interaction at different HPA contents was previously discovered in [22], where it is also indicated that in the acid-acid type of interaction, HPA stability depends on the percentage of HPA deposition on the carrier: at low HPA contents (5–10 wt. %) on the surface of silicon dioxide, HPA of the 12th row is destroyed and HPA of the 6th row is formed, whereas with an increase in the content of HPA on the support (10–25 wt. %), the structure of HPA is retained.

Conclusions

Summarizing the above results, we can make the assumption that specific surface area and dispersion phosphomolybdenum heteropoly acid–titanium oxide catalytic system are not key factors responsible for high catalytic activity in the process of obtaining diisopropyl ether (there is no clear correlation to this effect). It was determined that the catalytic activity of titanium dioxide samples before and after the introduction of heteropoly acid has a different nature (the ether input in the presence of heteropoly acid-containing samples is higher, reaches maximum values in a shorter period of time and is characterized by greater stability). It should be noted that the activity of heteropoly acid-containing titanium oxide catalytic system samples is determined by the ratio of meta-titanic acid hydrate and metaphosphoric acid, when a quantitative increase in the latter entails a decrease in new surface active centers, or their rearrangement. Presumably meta-titanic and metaphosphoric acids are formed when applying more than 7 % wt. phosphomolybdenum heteropoly acid and represent a surface complex polymer compound.

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Гетеропол қышқылы – титан оксиді жүйесінің қатысуымен изопропил спиртінің конверсиясы

Гетерополий қышқылы – титан диоксиді жүйесінің фазалық және текстуралық қасиеттерін зерттеу үшін заманауи физикалық-химиялық әдістер кешені қолданылды (рентгендік фазалық анализ, азоттың аз температуралық адсорбциясы, сканерлеуші электронды микроскопия, элементтік анализ). Титан диоксидінің каталитикалық белсенділігінің жоғарылауына әкелетін фосформолибден гетерополий қышқылының оңтайлы мөлшері 7%-ды құрайтыны анықталды: диизопропил эфирінің шығымы жоғары, қысқа мерзімде максималды мәндерге жетеді және сынамалар тұрақты. Құрамында фосформолибден гетерополий қышқылы бар үлгілердің белсенділігі электронды-донорлық қасиеттерін көрсететін белсенді орталықтардың жаңа типтерінің пайда болуымен байланысты деп саналады (гетерополий қышқылының М=О октаэдрасының сыртқы фрагменттерінің шеткі оттегі атомдары). Құрамында фосформолибден гетерополий қышқылы бар үлгінің каталитикалық белсенділігінің 7%-дан көп төмендеуі беткі қабаттағы метафосфор қышқылының түзілуіне байланысты болады және белсенді орталықтардың төмендеуіне әкеледі.

Кілт сөздер: изопропил спирті, титан диоксиді, фосформолибден гетерополий қышқылы, фазалық құрам, морфология, катализ, диизопропил эфирі, текстуралық қасиеттері, метатитан қышқылы, метафосфор қышқылы.

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Преобразование изопропилового спирта в присутствии системы гетерополикислота – оксид титана

Комплексом современных физико-химических методов (рентгенофазовый анализ, низкотемпературная адсорбция азота, сканирующая электронная микроскопия, элементный анализ) изучены фазовые и текстурные свойства системы гетерополикислота – диоксид титана. Установлено, что оптимальным содержанием фосформolibденовой гетерополикислоты, которое приводит к повышению каталитической активности диоксида титана, является 7 % масс.: выход диизопропилового эфира выше, достигает максимальных значений за более короткий промежуток времени, а образцы характеризуются большей стабильностью. Выдвинуто предположение, что активность фосформolibденовой гетерополикислотно-содержащих образцов связана с появлением активных центров нового типа, которые проявляют повышенные электронно-донорные свойства (концевые атомы кислорода внешних фрагментов октаэдров $M=O$ гетерополикислоты). Падение каталитической активности образцов с содержанием фосформolibденовой гетерополикислоты свыше 7 % масс. связано с образованием поверхностной метафосфорной кислоты и влечет за собой уменьшение активных центров.

Ключевые слова: изопропиловый спирт, диоксид титана, фосформolibденовая гетерополикислота, фазовый состав, морфология, катализ, диизопропиловый эфир, текстурные свойства, метатитановая кислота, метафосфорная кислота.

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