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**CONVERSION OF ISOPROPYL ALCOHOL TO
DIISOPROPYL ETHER IN THE PRESENCE
PHOSPHORMOLYBDENUM HETEROPOLY ACID**

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ABSTRACT

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GENERAL DESCRIPTION OF WORK

Relevance of the topic. Isopropyl alcohol is considered one of the largest petrochemical products. Its industrial production in Azerbaijan began in 1966 on the basis of the Sintezkauchuk plant. In 2020, on the recommendation of President Ilham Aliyev, the plant for the production of absolute isopropyl alcohol at the Ethylene-Polyethylene Plant of SOCAR (State Oil Company of the Republic of Azerbaijan) JSC Azerkimya was reconstructed, after which the daily output of this product reached 60 tons.

The expansion of the market for the sale of isopropyl alcohol is related not only with its traditional areas (effective solvent, production of perfumery and cosmetics, hygiene products, etc.), but also with the possibility of using it as an intermediate product or petrochemical raw materials, in particular, to obtain diisopropyl ether (DIPE).

DIPE is considered one of the most widely used compounds of its class. It is used as a solvent in the processes of oil dewaxing, acid extraction, oil production, chromatographic analysis, medicine, paint and varnish industry, household chemicals, printing and a number of other areas. One of them is the use of DIPE as a promising oxygen-containing additive to gasoline. Therefore, the selection of effective catalysts for the conversion of isopropyl alcohol into valuable petrochemical products continues to attract the close attention of catalytic chemists.

It should be noted that, along with the generally recognized catalytic systems used in the process of converting isopropyl alcohol into oxygen-containing compounds, periodic literature contains information about the prospects of carrying out this process in the presence of heteropoly acids (HPAs).

The use of CHP in catalysis is an intensively developing direction. Significant progress has been made in the study of the catalytic properties of not only bulk but also supported HPAs. It is known that in some cases, when HPA is applied to a carrier, their availability increases, but the strength and nature of the acid sites change. Literature data on the change in some properties of specific supported HPA-con-

taining systems are contradictory on the retention of the structure, thermal stability of HPA after application, and chemical interaction with the carrier. The reason for these changes is not clear yet..

In this regard, conducting comprehensive and detailed studies of the catalytic and physicochemical properties of the supported phosphorus-molybdenum CHP in the process of converting isopropyl alcohol into DIPE using a wide range of instrumental methods is undoubtedly an urgent task, the solution of which will contribute to a deep understanding of the manifested properties and promote the development this promising direction.

The purpose of this work consisted in identifying patterns that relate the catalytic properties of samples obtained by applying phosphorus-molybdenum HPA samples to aluminum oxide and titanium oxide in the process of converting isopropyl alcohol into DIPE, with their composition, structure, textural, spectroscopic properties, and kinetic patterns.

The work included a number of successive stages:

- study of the catalytic activity of phosphorus-molybdenum HPA deposited on alumina (γ - and η -) and titanium oxide in the reaction of converting isopropyl alcohol into DIPE;
- study of the structure of phosphorus-molybdenum HPA deposited on aluminum oxide (γ - and η -) and titanium oxide using modern physical and chemical methods;
- revealing patterns that relate the nature of the support, the composition and structure of the synthesized catalytic systems with their catalytic properties;
- study of the kinetic parameters of the conversion of isopropyl alcohol to DIPE in the presence of supported phosphorus-molybdenum CHP.

Scientific novelty. A relationship has been established between the nature of the support, the composition and structure of the synthesized phosphorus-molybdenum-heteropolyacid-supported catalytic systems, which exhibit their catalytic properties during the conversion of isopropyl alcohol to DIPE.

Comparative study of the catalytic properties of η -Al₂O₃, γ -Al₂O₃ and TiO₂ containing from 5 to 13 wt. phosphomolybdenum heteropolyacid, made it possible to establish that 7% H₃PMo₁₂O₄₀/TiO₂ showed the highest activity in the process of converting isopropyl alcohol to DIPE: at a temperature of 150°C, the yield of DIPE was 21.6% with a selectivity of 77.1%.

For the first time, based on the results of physicochemical studies, the differences in the catalytic activity of the H₃PMo₁₂O₄₀/ η -Al₂O₃ and H₃PMo₁₂O₄₀/ γ -Al₂O₃ systems are substantiated. It has been established that, unlike γ -Al₂O₃ and TiO₂, after applying phosphorus-molybdenum CHP to η -Al₂O₃, it does not retain its integrity.

The phase, textural, and morphological properties of the H₃PMo₁₂O₄₀/TiO₂ system were studied using a complex of modern physicochemical methods, as a result of which it was found that the fineness and pore size are not the key factors responsible for the catalytic activity exhibited during the conversion of isopropyl alcohol to DIPE. It was found that the increased activity of 7% H₃PMo₁₂O₄₀/TiO₂ is associated with both the presence of phosphomolybdic acid and the appearance of metaphosphoric acid, which is formed due to the combination of surface PO₄ tetrahedra into rings.

The kinetic parameters of the conversion of isopropyl alcohol to DIPE in the presence of TiO₂ and the 7% H₃PMo₁₂O₄₀/TiO₂ system were calculated.

The practical significance of the work. The studies carried out are of considerable scientific interest, since they made it possible to reveal a correlation between the nature of the carrier and the type of interaction with phosphorus-molybdenum HPA. At the same time, this work is also of practical importance, since it creates wide possibilities for creating new supported heteropoly acid-containing systems with a set of specified physicochemical and catalytic properties, which is of great interest for the development of highly efficient catalysts for the production of oxygen-containing compounds on their basis.

Approbation of work. The main results of the research were reported and discussed at a number of international and republican conferences: ITWCCST (Azerbaijan, 2017), Fundamental and applied research in the field of chemistry and ecology (Russia, 2018), Nagiyev

readings (Azerbaijan, 2018), Actual problems of modern chemistry (Azerbaijan, 2019), Conference On Actual Problems Of Chemical Engineering (Azerbaijan, 2020), ROSKATALIZ (Russia, 2021).

Publications. The main results on the topic of the dissertation were published in 15 scientific papers, including 8 articles in journals recommended by the Higher Attestation Commission.

The volume and structure of the dissertation. The dissertation consists of an introduction, 5 chapters, 4 conclusions and a list of cited 192 literature, including titles. The work is presented on 200 pages, contains 25 tables and 38 figures.

MAIN CONTENT OF THE WORK

Aluminium oxide

Catalytic properties of aluminum oxide. Figure 1 shows the dependences of the effect of the process duration on the degree of conversion of isopropyl alcohol in the presence of $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\eta\text{-Al}_2\text{O}_3$ catalysts. The obtained results indicate that the presence of HPA has an ambiguous effect on the activity of the catalyst: the sample containing the minimum amount (5%) of HPA is characterized by a low degree of alcohol conversion, however, with an increase in the content of HPA in the catalyst composition to 7–10%, the picture changes dramatically to opposite.

The maximum degree of conversion of raw materials was noted with the participation in the process of 10% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing sample and amounted to 56.3%. A sharp decrease in the degree of alcohol conversion in the presence of 13% HPA-containing sample, is probably due to its almost instantaneous deactivation, therefore, we do not take it into account in further discussion.

Modified samples containing 5, 7 and 10% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\eta\text{-Al}_2\text{O}_3$ -catalysts showed high selectivity for oxygen-containing products (table 1): the maximum selectivity for 7% HPA-containing sample (3.5 times higher than unmodified). A characteristic feature of the influence of CHP is also the presence of acetone in the reaction

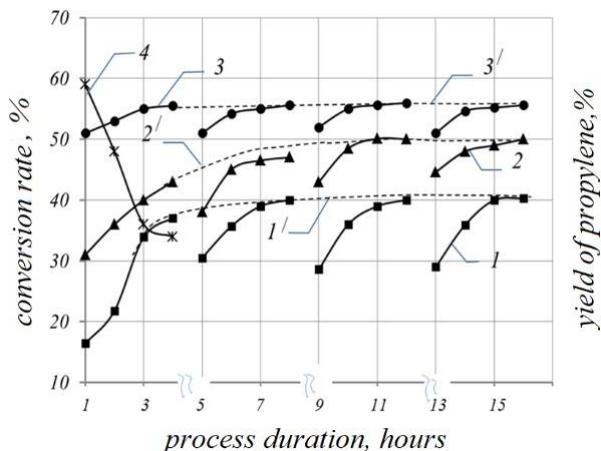


Fig.1. The effect of the process duration on the degree of isopropyl alcohol conversion in the presence of HPA/ η - Al_2O_3 catalysts, in which the content of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$:

fifteen%; 2 - 7%; 3 - 10%; 4 – 13% (dashed lines refer to the corresponding trend lines at the content of HPA 1/– 5%; 2/ – 7%; 3/ – 10%; 4/ – 13%).

$T = 230^\circ\text{C}; \omega = 750 \text{ h}^{-1}$.

products (in the presence of the initial sample η - Al_2O_3 acetone was not formed).

Taking into account the data obtained above, when studying the catalytic properties of HPA-containing η - Al_2O_3 catalysts, the amount of supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ on γ - Al_2O_3 was 7%. The dependence of the composition of the products of the conversion of isopropyl alcohol on temperature in the presence of γ - Al_2O_3 before and after the modification of HPA is presented in Table 2.

Prior to modification, γ - Al_2O_3 exhibits weak catalytic activity at low temperatures—the degree of conversion at 150°C is 3.5%. With an increase in temperature to 200 and 250°C , this index increases to 17 and 47.6%, respectively. It is interesting to note that in the presence of supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\gamma$ - Al_2O_3 catalysts, the activity of the catalyst is strikingly different:

Table 1

**Effect of H₃PMo₁₂O₄₀/η-Al₂O₃ Catalyst Composition
on process indicators**

Katali- congestion	TO, %	Durat ion, hour*	SKS, %	α acetone , % vol.	α ether, % vol.	Ratio	
						C ₃ H ₆ / KSS	C ₃ H ₆ O/ C ₆ H ₁₄ O
η-Al ₂ O ₃ (without GPC)	42	8	14.9	-	6.25	5.72	-
η-Al ₂ O ₃ + 5% HPA	44.6	7	46.6	16.3	4.5	1.44	3.62
η-Al ₂ O ₃ + 7% HPA	50.1	11	52.1	17.4	8.7	0.92	2.0
η-Al ₂ O ₃ + 10% HPA	56.3	3	40.1	14.5	7.3	1.49	1.99
η-Al ₂ O ₃ + 13% HPA	59.2	1	28.5	10.2	6.7	2.50	1.52

*the indicated degree of alcohol conversion (K) and the duration of the process correspond to the highest yield (α) of oxygen-containing products (CCC) for this sample; T=200°C; ω = 750 h⁻¹.

Table 2

**Effect of the H₃PMo₁₂O₄₀/γ-Al₂O₃ composition of the
catalyst on process indicators**

Catalyst	Conditions experiment		Degree of conversion, %	Output, %			
	Pace., °C	Durati on, hour		Ether	Aceto ne	Gek- sen	Propylen e
γ- Al ₂ O ₃	150	6	3.5	1	1.7	0.1	0.7
	200	3	17.1	3	0.7	1.3	12.0
	250	5	47.6	4.7	0.2	18.2	24.5
HPT/ γ- Al ₂ O ₃	150	4	15.6	0.7	0.1	0.2	14.6
	200	3	38.6	12.5	1.2	0.2	24.7
	250	2	60.7	0.9	8.6	1.9	49.3

* indicators correspond to the highest conversion; T=200°C; ω = 750 h⁻¹.

the degree the conversion at 150 and 200°C increases by more than 4 and 2 times, respectively, and at 250°C, by more than 25%. It should also be noted both the qualitative and quantitative changes in the composition of the reaction products: at 150°C, only propylene is formed; at 250°C, propylene and DIPE; at 300°C, propylene and acetone.

However, a comparative analysis of the obtained results of the conversion of isopropyl alcohol on modified η - and γ -alumina revealed a higher activity of supported η -Al₂O₃, in particular, in terms of the selectivity of oxygen-containing compounds (52.1% for η - and 14.2% for γ -Al₂O₃), and also the duration of the run (Fig. 3.5).

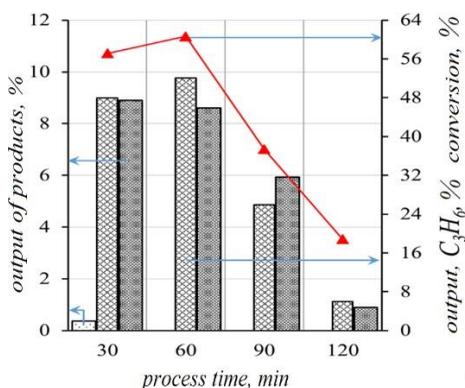
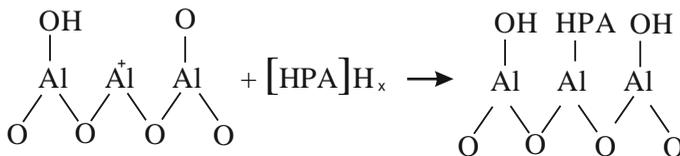


Fig.2. Influence of Process Time on the Conversion and Yield of Propylene, Acetone, and Ether in the Presence of a Sample $H_3PMO_{12}O_{40}/\gamma-Al_2O_3$ ($T=200^\circ C; \omega = 750 h^{-1}$):



- ether;
- acetone;
- propylene.

Under the condition of the same chemical nature of the carrier, the main difference between the mechanisms of interaction, and as a result of the formation of the active surface of the two modifications, in our opinion, is the nature of the active centers η - and γ -Al₂O₃. It is known that the η -modification is characterized by increased Lewis acidity. It is these active centers that are able to pull the heteropoly anions of the acid towards themselves, destroying its structure:



In the case of $\gamma\text{-Al}_2\text{O}_3$, according to the literature, this modification contains the largest number of weak Brönsted and a small number of Lewis acid sites (mainly 80-90% weak), as well as strong and medium basic centers (practically every oxygen atom is the main center). Under these conditions, the most probable is the "grafting" of HPA to the surface due to the formation of hydrogen bonds between the surface OH groups and the oxygen atoms of the carrier, on the one hand, and electron-donating substituents and protons of the secondary structure, on the other. Electrodonor atoms in the structure of the 12th row HPA can be the terminal oxygen atoms of the outer fragments of the $\text{M}=\text{O}$ octahedra. Since there are 12 of them in each molecule, and there are 3 hydrogen atoms, the sorption of HPA on the carrier surface will be "multipoint", that is, strong.

Thermal properties of aluminum oxide. Based on the fact that HPAs are crystalline hydrates, we set the task of revealing the relationship between the thermal stability of $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ and the thermal effect caused by the destruction and recrystallization of the heteropolyanion - the removal of structural water, the endo effect at a temperature of 438.6°C (Table 3).

It is noteworthy that the temperature effects associated with the removal of structural water and decomposition of the anion were not observed in the samples deposited with $\text{H}_3\text{PMO}_{12}\text{O}_{40}/\eta\text{-Al}_2\text{O}_3$. These results are in good agreement with the data of XRD studies (see below), indicating the absence of HPA on $\eta\text{-Al}_2\text{O}_3$.

Table 3

Characterization of effects according to the differential thermal analysis

Sample	thermal effect								
	I			II			III		
	Start	Max	Con.	Beginning	Max	Con.	Beginning	Poppy	Con.
GIC	Endo-			Endo-			Exo-		
	162	251	391		438		435	438	718
HPA/ η -Al ₂ O ₃ before catalysis	Endo-			-			Exo-		
	173	256	334				337	478	770
HPA/ η -Al ₂ O ₃ after	Endo-			-			Exo-		
	165	236.6	292				492	586.3	692
HPA/ γ -Al ₂ O ₃ before catalysis	160	209	302		358		482	583	880
HPC/ γ -Al ₂ O ₃ after				-					

The temperature of removal of structural water from the deposited γ -Al₂O₃ is almost 80°C lower than that noted for the individual H₃PMo₁₂O₄₀, indicating the interaction between the carrier and HPA. The difference between the DTA results of H₃PMo₁₂O₄₀/ γ -Al₂O₃ before and after participation in the catalysis process is that the latter does not have effects associated with the thermal transformation of CHP. This may be due to a factor that is difficult to control: partial washing away of the acid from the carrier surface by the reaction stream. In this case, the drop in catalyst activity during the formation of oxygen-containing compounds after 210 min is expected.

Phase analysis of aluminum oxide. In the X-ray diffraction pattern of 7% H₃PMo₁₂O₄₀/ η -Al₂O₃, there were no reflections indicating the presence of HPA, the appearance of new peaks at 12.9°, 48.73° and 58.96° 2 θ , which belong to molybdenum hydroxide, was noted. No peaks of phosphorus were observed in the diffraction pattern, which may be due to either its small amount or its incorporation into

alumina. These changes occur against the background of a noticeable decrease in the coherent scattering region, which indicates the dispersion of the system.

Textural properties of aluminum oxide. The surface morphology of η - Al_2O_3 and $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\eta$ - Al_2O_3 catalysts was studied by scanning electron microscopy. η - Al_2O_3 particles are close-packed large agglomerates - isometric spherical shapes with a bumpy surface (Fig. 3).

After the introduction of the HPA, the morphology and size of these formations changed. They collapsed and are now represented by 2 types (see the particle size distribution): in the vast majority - highly dispersed particles of about a spherical shape with a size of less than 1 μm and their aggregates, the size of which is more than 50 μm (the formation of fine particles is in good agreement with the results of X-ray phase analysis) and particles with a small diameter (less than 0.1 μm), respectively (Fig. 3). Their loose packing provides a higher surface area, which, as mentioned at the very beginning, is one of the necessary conditions for the efficient use of HPA in heterogeneous catalysis.

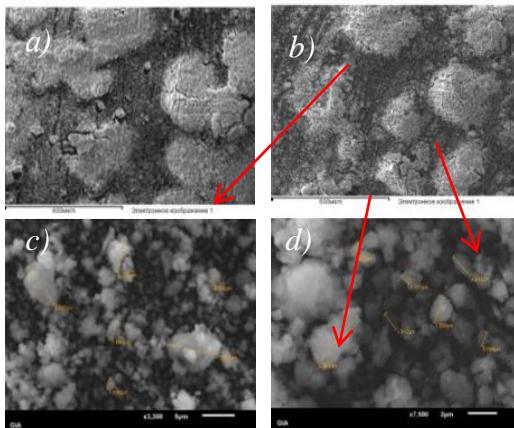


Fig.3. Micrographs of η - Al_2O_3 (a), general view of 7% $\text{H}_3\text{Pmo}_{12}\text{O}_{40}/\eta$ - Al_2O_3 (b), structure of individual particles (c, d).

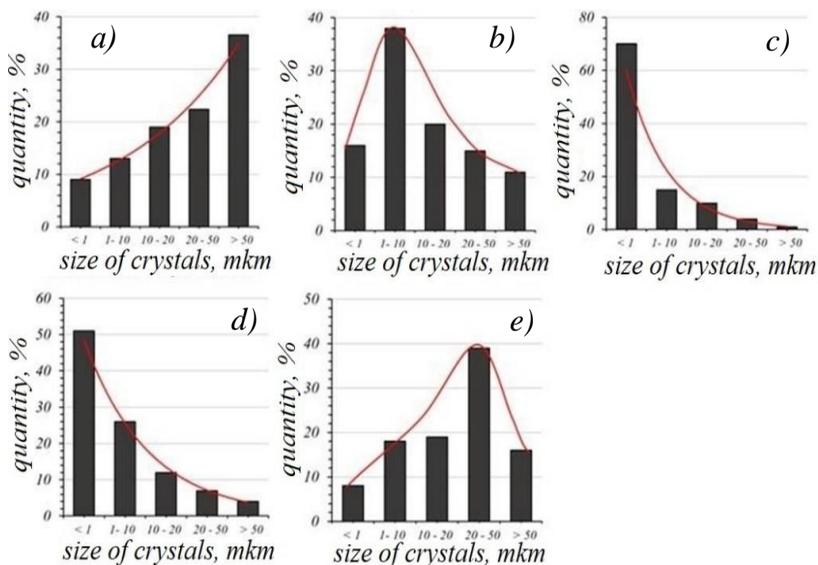


Fig.4. Particle size distribution histogram: a – initial η -Al₂O₃; b – 5% H₃PMo₁₂O=/ η -Al₂O₃; c – 7% H₃PMo₁₂O₄₀/ η -Al₂O₃; d-10% H₃PMo₁₂O₄₀/ η -Al₂O₃; e – 13% H₃PMo₁₂O₄₀/ η -Al₂O₃.

Based on microphotographs, histograms of particle size distribution were constructed (Fig. 4). As can be seen, the nature of the histograms of 7 and 10% H₃PMo₁₂O₄₀-containing samples have a certain similarity. The particles of these catalysts have an average size of less than 1 micron; the corresponding dispersion is above 50%. In all likelihood, there is some critical concentration of the modifier, the threshold value of which is 10%, after which there is a sharp change in particle size distribution and catalytic properties..

Taking into account the fact that, as shown above, the highest activity and selectivity for oxygen-containing hydrocarbons for the series of HPA/ η -Al₂O₃ catalysts under study was noted precisely for highly dispersed 7-10% HPA samples, this reaction is structure-sensitive.

Titanium dioxide

Catalytic properties of titanium dioxide. Over the entire studied temperature range, the conversion of isopropyl alcohol in the presence of $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ increased the stronger, the higher the HPA content. The minimum conversion value is noted for a sample containing 5% of the mass. 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. sample, which reaches 54%, which significantly exceeds the others. With an increase in temperature to 250°C, the conversion of 7 and 10% HPA-containing catalysts becomes almost the same (from 71 to 76%) (Fig. 5).

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

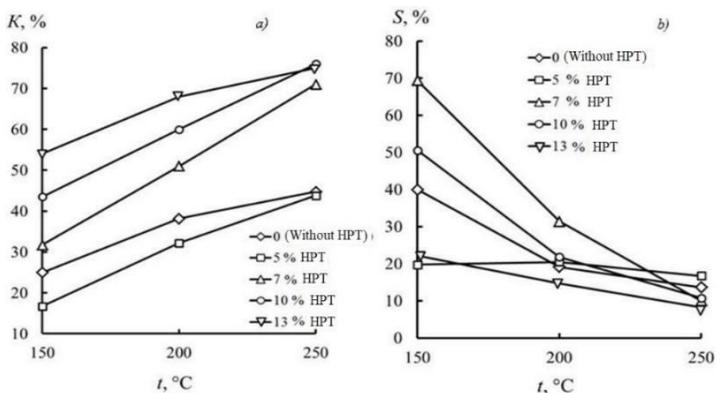


Fig. 5 Influence of the catalyst composition on the conversion (a) of isopropyl alcohol and the selectivity (b) of formation DIPE. $T = 150^\circ\text{C}$; $\omega = 750 \text{ h}^{-1}$.

Table 4

Effect of duration on process performance

Duration, hour	Catalyst Composition									
	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

Note: temperature 150°C; ω = 750 h⁻¹. Designations: S - selectivity, α is the output of DIPE.

According to Table 4, 7% H₃PMo₁₂O₄₀/TiO₂ exhibits the maximum activity: the DIPE yield from the 2nd to the 4th hour of each operation interval is 20.5–22% with an ester formation selectivity of 49.2–77.1%.

Table 5

Characteristics of thermal effects H₃PMo₁₂O₄₀/TiO₂

Sample	thermal effect								
	I			II			III		
	Start	Max	Kon	Start	Max	Con.	Begin ning	Popp y.	Con.
HPA/TiO ₂ before catalysis	Endo-			Endo-			Endo-		
	157	245	440	280	401	542	500	647	854
HPA/TiO ₂ after	Endo-			Endo-			Endo-		
	160	251			406	574	427	562	850

Thermal properties of titanium dioxide. Based on thermal analysis results 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ (Table 5), the presence of the same thermal effects in the deposited one as in the individual HPA was found, i.e. preservation of its structure after deposition on titanium dioxide (in contrast to the samples deposited on alumina). The main result of the synchronous TG/DTA analysis of a sample of HPA-containing titanium oxide, after participation in the catalytic process, was the almost complete coincidence of thermal effects with the sample before catalysis. This indicates the stability and preservation of the individual structural forms of HPA-containing titanium oxide under the reaction conditions. Also, the results obtained in the course of thermal analysis indicate a high resistance of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing titanium dioxide to the formation of coke on its surface, which is also one of the conditions allowing

Phase analysis of titanium dioxide. Figure 6 shows diffraction patterns of titanium dioxide, as well as modified samples containing 5.7, 10 and 13% phosphomolybdic acid. As can be seen from Fig. 6a, 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 -ty samples).

With an increase in the content of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ to 7% wt. (Fig. 6 c) along with the bands characteristic of anatase, the diffraction pattern shows the appearance of new reflections corresponding to five new phases: 56.32° 2 θ – TiMoO_4 ; 21.7, 36.56 and 44.39 °2 θ – $\text{H}_2\text{Ti}_5\text{O}_{11} \text{H}_2\text{O}$; 10.89, 15.53, and 31.02° 2 θ —HPA ($\text{H}_3\text{PMo}_{12}\text{O}_{40} 21\text{H}_2\text{O}$); 26.86, and 52.37° 2 θ – $\text{H}_3\text{P}_3\text{O}_{10} 2\text{H}_2\text{O}$, as well as 32.01 and 47.04°2 θ - PO_4 ; in addition, a decrease in the crystallinity of the sample was noted.

The last of the investigated, 13% HPA-containing samples (Fig. 6e), of the previously noted six phases, has reflections related to TiO_2 (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), $\text{H}_2\text{Ti}_5\text{O}_{11} \text{H}_2\text{O}$ (7.98, 21.49, 36.19° 2 θ), $\text{H}_3\text{PMo}_{12}\text{O}_{40} 21\text{H}_2\text{O}$ (10.92, 15.33, 18.46 and 31.02° 2 θ). In addition, this sample is also characterized by the highest amorphism. Undoubted interest is the fact that the PO_4 phase, noted in 7% of the sample, was not detected in subsequent samples.

Summing up the results of the study and based on the data obtained, as well as considering the nature of the modifier, it can be assumed that an increase in activity of 7% wt. $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ - containing titanium dioxide is associated with the appearance of a new type of active centers, which exhibit enhanced proton-donor and 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 will be confirmed in the course of thermal and phase analysis), both the hydrogen and the oxygen atom included in the HPA can act as such centers. It is likely that the above-mentioned low ether activity of modified titanium dioxide at a content of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ below 7% is associated with an insufficient concentration of new active centers.

Probably, the above-mentioned low activity of the modified titanium dioxide on ether at the content $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ up to 7% is associated with insufficient concentration of new types of active centers. Explain the marked drop in catalytic activity when the content of CHP is above 10% wt. can be based on the possibility of the formation 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 tetrahedra PO_4 into rings. An indirect confirmation of the formation of metaphosphoric acid is the appearance of its additional reflection at $22.5^\circ 2\theta$ in the 13% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ sample.

Textural properties of titanium dioxide. The data obtained in the study of the textural characteristics of $\text{H}_3\text{PMo}_{12}\text{O}_{40} / \text{TiO}_2$ are shown in Table 6, from which it follows that the samples have a specific surface area of 40 to 57 m^2/g and a total pore volume of 0.16 to 0.24 m^3/g . At the same time, the initial unmodified titanium dioxide sample is characterized by a maximum specific surface area of 57 m^2/g and also the highest total pore volume of 0.24 m^3/g .

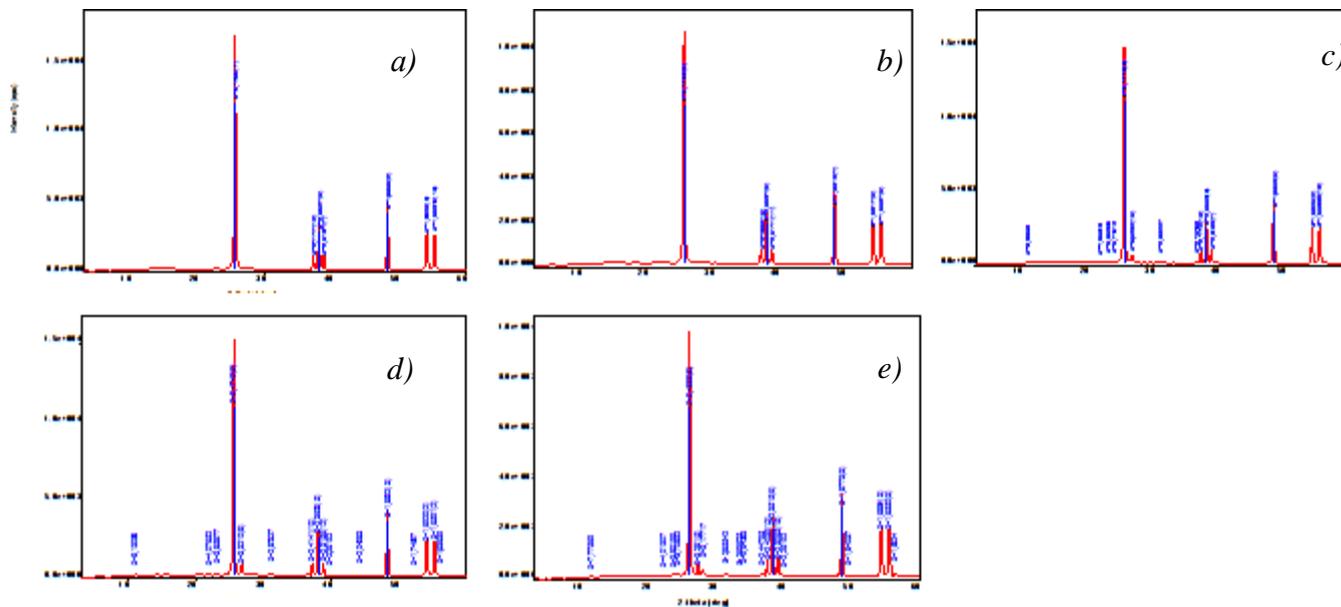


Fig. 6. X-ray diffraction patterns of titanium dioxide: original, not containing HPA (a); containing H₃PMO₁₂O₄₀ : 5% wt. (b), 7% wt. (c), 10% wt. (g) and 13% of the mass.

Table 6

Textural properties of H₃PMo₁₂O₄₀ / TiO₂ samples

Indicator	Content of CHP, %				
	*	5	7	10	13
S _{ss}	57	51	47	42	40
V _{sp}	0.24	0.22	0.21	0.21	0.16
P _{cat}	0.008	0.003	-	-	-
P _{true}	3.80	3.66	3.54	3.51	3.40
ρ _{apparent}	0.8	0.83	0.85	0.88	0.92
ρ _{bulk}	0.79	0.72	0.69	0.64	0.6
ε	0.2625	0.3373	0.3647	0.4091	0.4348
R _□	0.64	0.64	0.63	0.63	0.63

Note: S_{sp} – specific surface area, m²/g; V_{sp} – specific pore volume, cm³/g; P_{cat} is the porosity of the catalyst, vol. %; ρ_{true}, ρ_{apparent} and ρ_{bulk} – true, apparent and bulk density, respectively, g/cm³; ε – layer porosity; P_□ – crushing strength, MPa.

After the introduction of the modifier, there is a tendency to decrease these indicators the more, the higher the content of H₃PMo₁₂O₄₀. Thus, the introduction of HPA leads to a decrease in the specific surface area 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 when the content of H₃PMo₁₂O₄₀ is up to 10 wt%, it is located mainly in smaller pores (pores <5 nm in size decrease up to 10 times compared to the initial titanium dioxide, table 6), which leads to their “overgrowth”, while while with an increase in the content of CHP over 10% of the mass. located in a wide pore space.

Porosity changes symbatically with the indicators of the total pore volume: it decreases with the introduction and subsequent increase in the amount of HPA, which, in our opinion, is associated with the above-mentioned blocking of small pores by the modifier. The absence of porosity indices for catalysts with an HPA content of more than 5% indicates that these samples are practically non-

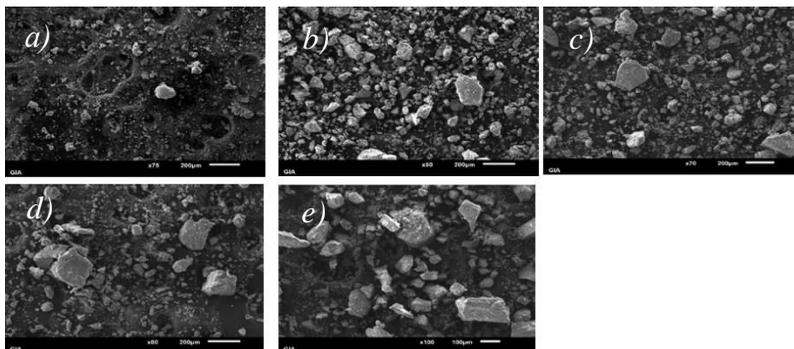


Fig. 7. Comparative SEM characteristics of titanium dioxide samples before (a) and after the introduction of CHP (b - 5% wt. HPA; c - 7% wt. HPA; d - 10% wt. HPA; e - 13% wt. HPA)

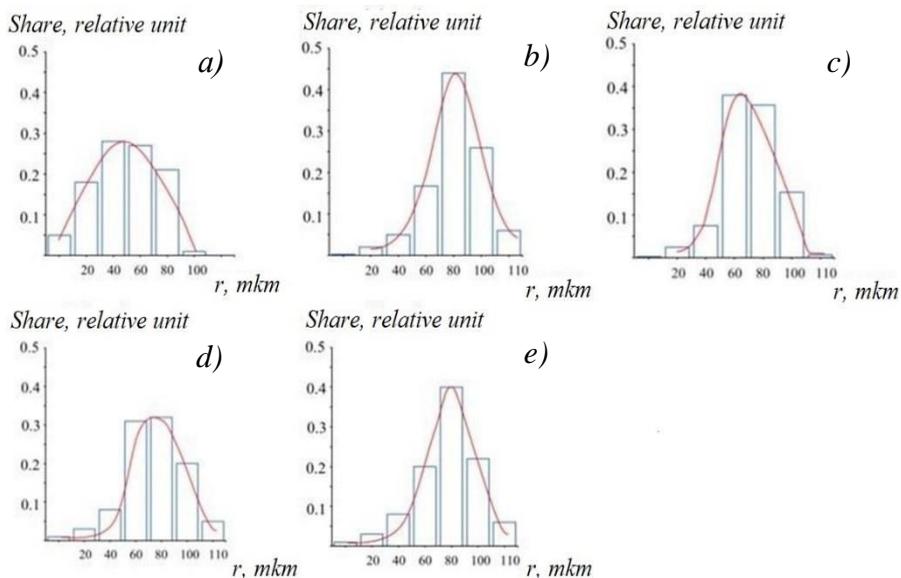


Fig 8 .Size distribution of crystallites of titanium dioxide samples before (a) and after the introduction of CHP (b - 5% wt. HPA; c - 7% wt. HPA; d - 10% wt. HPA; e - 13% wt. HPA)

porous. The increase in porosity can be explained by an increase in the size of aggregates, a change in their packing density, and entrainment of the free space between them.

The specific surface of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing titanium dioxide samples is more than 5 times less than the corresponding analogs deposited on aluminum oxide. It is known that the specific surface area of catalysts depends on the average pore diameter and fineness. The specific pore volume of the deposited titanium dioxide samples is characterized by significantly lower values (almost 4 times less) than those of the deposited aluminum oxide samples. Considering that the activity of the latter is inferior to titanium dioxide, a conclusion follows about the secondary role of the inner surface in the activity exhibited by titanium dioxide. In addition, the increased stability of the catalytic activity of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing samples of titanium dioxide compared to aluminum oxide can also be associated with lower porosity and the predominance of larger pores.

Figure 7 shows SEM images of titanium dioxide samples before and after injection of various amounts of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. As can be seen, the surface of the initial titanium dioxide is represented by numerous isolated crystallites of irregular shape, mainly 21–60 μm in size. It should be noted that without exception, all $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing samples are mainly characterized by the content of relatively larger crystallites (41–80 μm).

Thus, the SEM image for 5% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ containing titanium dioxide is characterized by clearly defined and well identifiable structural elements (80 μm). At the break, large blocks with a complex structure stand out; it is possible to fix the presence of clear boundaries in the blocks, apparently formed during the preparation process. When 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is introduced, the catalyst surface is represented by smaller agglomerates, predominantly 60 μm in size and smaller (Fig. 8). The content of 10% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ leads to the appearance of aggregates in places due to compaction of small particles. Their dimensions are equally represented by both 60 and 80 μm particles. There is a tendency towards enlargement of surface particles. And finally

The titanium dioxide obtained by adding 13% $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is characterized by low dispersion and the virtual absence of micropores,

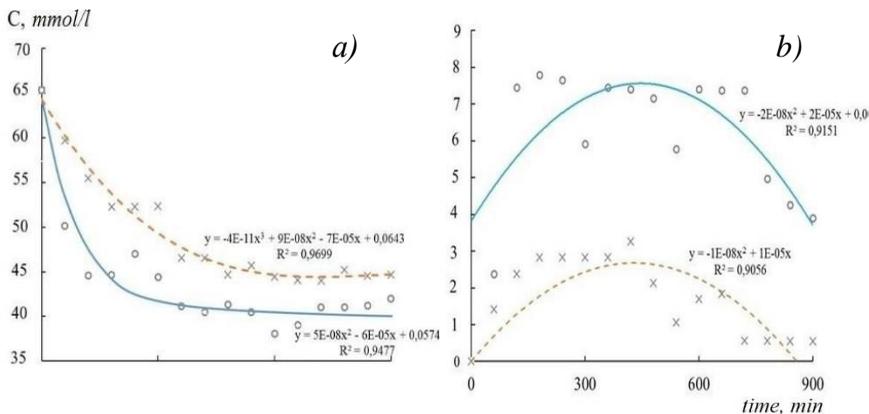
and also has a reduced catalytic activity in the reaction of intermolecular dehydration of isopropyl alcohol. Considering that the preparation of all the studied samples was carried out under identical conditions (temperature and duration of calcination), the change in particle size cannot be associated with these factors, but only with the influence of the modifier - $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.

Summing up the presented results of $\text{H}_3\text{PMo}_{12}\text{O}_{40} / \text{TiO}_2$ studies, we can make the following assumptions:

- the specific surface area and dispersion of the 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40} / \text{TiO}_2$ sample are not the key factors responsible for its high catalytic activity; the reaction of converting isopropyl alcohol to DIPE is not structure sensitive;
- the catalytic activity of titanium dioxide samples before and after the introduction of phosphomolybdic acid has a different character (the yield of ester in the presence of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing samples is higher, reaches maximum values in a shorter period of time and is characterized by greater stability);
- The activity of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -containing samples is determined by the presence of PO_4 , metatitanic acid hydrate, and metaphosphoric acid, while a quantitative increase in the latter leads to a decrease in new surface active centers or their rearrangement.

Kinetics of isopropyl alcohol conversion in the presence of TiO_2 and $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$

Within the framework of the presented work, studies were carried out to study the kinetics of intermolecular dehydration of isopropyl alcohol in the presence of pure titanium dioxide, as well as its modified 7% - $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ form (Fig. 9).



**Fig.9. Kinetic dependences of the concentration of isopropyl alcohol (a) and diisopropyl ether (b) on the duration of the process in the presence of TiO_2 and 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$
 $T = 150^\circ\text{C}$ and $\omega = 750 \text{ h}^{-1}$**

Table 7
The effect of temperature on the conversion of isopropyl alcohol in the presence of $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$

temperature, K	K, %	Selectivity mol %			Yield %		
		DIPE	Propen	Aseton	DIPE	Propen	Aseton
373	21	70.5	6.6	0.6	14.8	1.4	0.8
423	34	60.7	11.4	2.8	23.7	6.8	0.9
453	46	53.3	16.2	6.0	24.5	7.4	2.7
483	53	32.2	18.3	6.8	17.0	9.7	3.6
513	64	14.5	21.4	7.2	9.3	13.7	4.6

For both types of catalysts, a monotonic increase in the concentration of the target product is observed with a deceleration to 300 and 120 min for $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ and TiO_2 , respectively. The highest concentration of diisopropyl ether was observed in the presence of modified titanium dioxide and amounted to almost 8 mmol/l.

Table 8

Effect of Isopropyl Alcohol Partial Pressure on Process Performance in the Presence of H₃PMo₁₂O₄₀/TiO₂

Partial pressure of alcohol, kPa	conversion, %	Selectivity mol %			Yield %		
		DIPE	Propen	Aseton	DIPE	Propen	Aseton
423K							
2.0	22.0	91.0	7.0	0.5	20.1	1.54	0.11
4.0	38.0	63.2	10.6	3.0	23.7	5.1	1.44
6.0	26.0	55.7	27.3	1.2	14.5	7.0	0.22
8.0	16.0	28.7	36.2	0.8	4.6	5.8	0.3
473K							
2.0	34.0	47.0	7.2	0.8	15.6	2.5	0.3
4.0	49.0	35.1	12.1	3.4	17.2	5.9	1.66
6.0	30.0	19.4	22.0	2.0	7.6	6.4	0.6
8.0	18.0	12.6	31.3	1.4	2.3	5.6	0.2
523K							
2	36.5	40.0	9.3	1.2	14.2	3.3	0.4
4	52.0	31.4	16.4	1.8	16.3	8.4	0.9
6	35.0	20.5	24.2	2.2	7.2	8.5	0.8
8	12.0	13.4	41.3	1.0	1.6	5.0	0.12

The results of the influence of temperature on the degree of alcohol conversion and the yield of reaction products depending on the partial pressure of the feedstock H₃PMo₁₂O₄₀/TiO₂:and TiO₂ are presented in Tables 7 and 8, respectively. Stepwise reaction mechanism for the conversion of isopropyl alcohol to diisopropyl ether in the presence of H₃PMo₁₂O₄₀/TiO₂:

1. C₃H₇OH + Z₁ ↔ Z₁ (C₃H₇OH)
2. C₃H₇OH + Z₂ ↔ (C₃H₇OH) Z₂
3. Z₁ (C₃H₇OH) + Z₂ (C₃H₇OH) ↔ (C₃H₇OC₃H₇) Z₁ + (HOH) Z₂
4. Z₂ (C₃H₇OH) ↔ Z₂ (C₃H₆) + Z₂ (HOH)
5. Z₁ (C₃H₇OC₃H₇) ↔ Z₁ (C₃H₇OH) + C₃H₆
6. Z₁ (C₃H₇OC₃H₇) ↔ Z₁ + C₃H₇OC₃H₇
7. Z₂(C₃H₆) ↔ Z₂+C₃H₆

8. $Z_2 (HOH) \leftrightarrow Z_2 + H_2O$
 9. $Z_1(HOH) \leftrightarrow Z_1 + H_2O$
 10. $Z_1 (C_3H_7OH) \leftrightarrow CH_3OCH_3 + Z_1(HOH)$

An analysis of the effect of temperature on the rate of consumption of the substrate made it possible to calculate the apparent activation energy of the process using both types of catalysts: TiO_2 and 7% $H_3PMo_{12}O_{40}/TiO_2$. The apparent activation energy was about 41 and 25 kJ/mol, respectively (Table 9).

Table 9

Influence of the catalyst composition on the kinetic parameters of the process

Compound catalyst	Kinetic parameters			
	ω 10-3 <i>mmol s⁻¹</i>	k_i 10-3, <i>s⁻¹</i>	Ea, <i>kJ/mol</i>	ti/2, <i>min</i>
TiO_2	0.265	0.229	41.919	50.18
7% $H_3PMo_{12}O_{40}/TiO_2$	1.407	0.722	25.251	15.92

Thus, the above results indicate that the application of phosphomolybdic acid to titanium dioxide affects not only the yield of reaction products, but also the kinetic and activation parameters of the conversion of isopropyl alcohol to DIPE. The presence of phosphomolybdic acid in the composition of the catalyst increases the rate of DIPE formation, reducing the activation energy of this reaction. The experimental material presented by us, taking into account published literature data, allowed us to propose a probable path (Fig. 10) for the formation of DIPE in the presence of 7% $H_3PMo_{12}O_{40}/TiO_2$: the formation of propylene occurs through the formation of associative, and DIPE - dissociative and associative complexes.

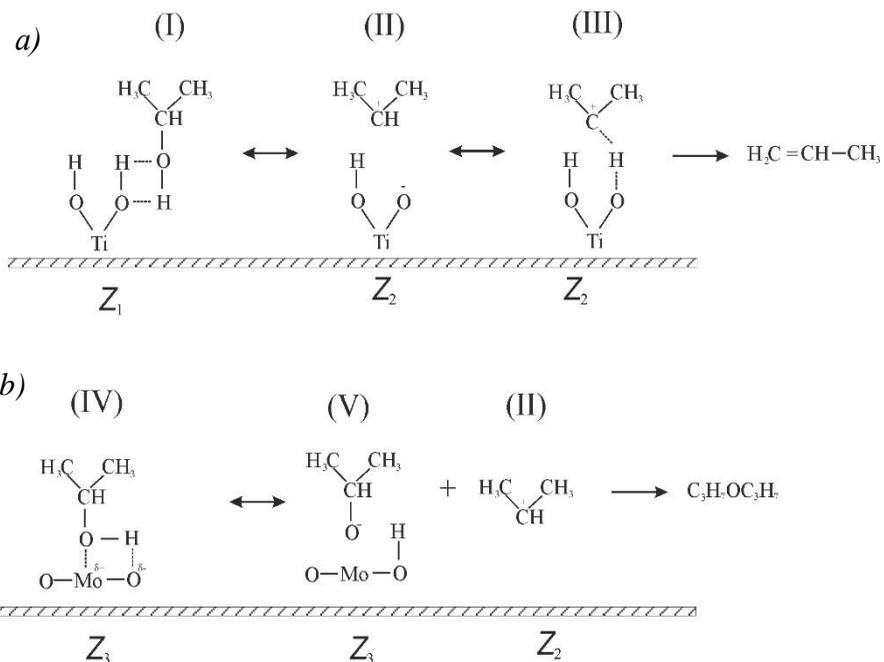
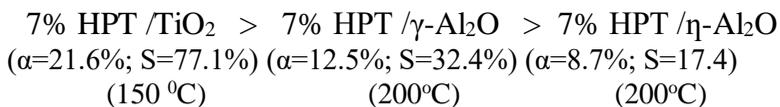


Fig.10.Suggested routes of diisopropyl ether formation in the presence of TiO₂ (a) and 7% H₃PMo₁₂O₄₀/TiO₂ (b).

FINDINGS

1. A comparative evaluation of the catalytic activity deposited on $\gamma\text{-Al}_2\text{O}_3$, $\eta\text{-Al}_2\text{O}_3$ and TiO₂ of phosphomolybdic acid was carried out. A relation has been established between the catalytic activity of the samples and the nature of the support and the content of the modifier, other things being equal. It is shown that the activity in the process of converting isopropyl alcohol into diisopropyl ether changes in the following order:



2. Based on the analysis of the totality of spectroscopic (IR-), structural (XRF), thermogravimetric data obtained during the dissertation, regularities were established that relate the catalytic and physico-chemical parameters of the synthesized systems:
 - it was found that after deposition of phosphomolybdic acid on $\eta\text{-Al}_2\text{O}_3$, in contrast to $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 , it does not retain its integrity; increased basicity of $\eta\text{-Al}_2\text{O}_3$ leads to neutralization of the heteropolyacid, weak acidity of $\gamma\text{-Al}_2\text{O}_3$ leads to multipoint grafting, and TiO_2 leads to physical adsorption;
 - it was found that the reason for the rapid deactivation of the sample of phosphorus-molybdic acid deposited on $\gamma\text{-Al}_2\text{O}_3$ is its physical washing off from the surface;
 - the stability of the catalytic properties and the preservation of the individual structural forms of phosphomolybdic acid on the surface of titanium dioxide, as well as the high resistance of the 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ catalyst to coke formation, were established;
 - it was found that the increased activity of 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ is associated not only with the presence of phosphomolybdic acid, but also with the appearance of PO_4 , metaphosphoric and metatitanic acids;
3. The combination of catalytic, morphological (SEM), and textural data indicates that the conversion of isopropyl alcohol to diisopropyl ether in the presence of phosphomolybdic acid on $\eta\text{-Al}_2\text{O}_3$ is structure-sensitive, but not on TiO_2 ;
4. The kinetic parameters of the conversion of isopropanol in the presence of TiO_2 ($n=1$; $E_a = 41 \text{ kJ/mol}$; $\omega = 0.265 \cdot 10^{-3} \text{ mmol} \cdot \text{s}^{-1}$) and the 7% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{TiO}_2$ system ($n = 1$; $\omega = 1.407 \cdot 10^{-3} \text{ mmol} \cdot \text{s}^{-1}$, $E_a = 25 \text{ kJ/mol}$).

The main results of the dissertation were published in the following articles and theses:

1. S.E.Yusubova, K.Y.Adjamov, E.A. Guseinova Transfer of isopropyl alcohol in the presence of aluminum oxide modified by phosphor-molybdenum heteropolyacid / ITWCCST 2017, Baku, ASOİA, Azerbaijan, p. 255.
2. S.E. Yusubova, E.A. Huseynova, K.Yu. Adjamov Catalytic activity of heteropolyacid-containing alumina in isopropyl alcohol conversion reactions / *Kimya problemleri*, 2018, No. 1 (16), - p. 127-135.
3. S.E. Yusubova, M.R. Salaev, E.A. Huseynova, K.Yu. research in the field of chemistry and ecology -2018". c. 101-103.
4. S.E. Yusubova, L.A. Mursalova, N.N. Bagirova, E.A. Huseynova Influence of the introduction of sulfate anions on the structure of titanium dioxide / *Proceedings of the scientific conference "Nagiev Readings"*, dedicated to the 110th anniversary of Academician M.F. Nagiyev, Baku, 2018. c. 317.
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6. S.E.Yusubova, K.Y. Adzhamov, E.A. Guseinova Catalytic transformations of isopropanol on aluminum η -oxide modified by heteropoly acid / *Azerbaijan Chemical Journal*, No. 3, -2019. c.32-41.
7. S.E. Yusubova, E.A. Huseynova, M. Al-Batbotti, M. R. Salaev, K. Yu. Müasir kimyanın aktual problemləri” mövzusunda beynəlxalq elmi konfrans, -2019, c. 344.
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12. S.E.Yusubova Fosformolobden heteropoliturşu-titan dioksid sisteminin bəzi spektroskopik xassələri "Neftin, qazın geotexnoloji problemləri və kimya" ETİ Elmi əsərləri, -2020. s.136-147
13. S.E. Yusubova, K.Yu. Adzhamov, E.A. Huseynova Catalytic transformations of isopropyl alcohol on the heteropolyacid-titanium oxide system / Bulletin of the Karaganda university, Chemistry Series No. 2(102) -2021. p. 53-62.
14. S.E. Yusubova, E.A. Huseynova, M.R. Salaev Catalytic activity of phosphomolybdic acid in the process of isopropyl alcohol conversion / "IV Russian Congress on Catalysis "ROSKATALIZ"" 20-25 sentyabr 2021 p.778.
15. S.E.Yusubova Obtaining diisopropyl ether in the presence of a heteropolyacid-titanium oxide catalyst / "Neftin, qazın geotexnoloji problemləri və kimya" ETİ Elmi əsərləri - 2021. 21-ci cild, s.350-359.



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