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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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Pt- AND Pd-CATALYSTS ON MODIFIED KAOLINITES IN THE REACTION OF N-HEXANE ISOMERIZATION

Abstract. The article presents the data on synthesis and properties of Pt and Pd catalysts supported on modified Ti^{4+} and Zr^{4+} kaolinites of two of Kazakhstan fields- Sarymsak, Ermakov (KS and KE), their catalytic activity in n-hexane isomerization, depending on temperature and composition of the catalyst. The elemental and phase composition of the synthesized catalysts, as well as their textural properties, are determined. It was indicated that the studied catalysts showed high activity and selectivity in the reaction isomerization of n-hexane with formation of mono- and disubstituted isohexanes and isoheptanes. The Pt catalysts supported on modified Zr^{4+} and Ti^{4+} kaolinites were exhibit higher isomerization activity compared to Pd-catalysts. Maximum conversion of n-hexane, equal to 43.2% and a yield of C_6 + C_7 isomers of 36.0% with selectivity for isomers of 93.3%, was observed on 0.35% Pt / Zr (5.0) HKS catalyst at 400 °C which can be recommended for further improvement.

Keywords: kaolinite, platinum, palladium, n-hexane, isomerization, selectivity, isomer yield, mono- and disubstituted isohexanes.

Introduction. Among the most important minerals are clays, which are widely used in various industries, agriculture and medicine [1]. It is known that the bentonite clays themselves are natural catalysts widely used in various refining processes [2, 3]. A characteristic feature of aluminosilicate catalysts (natural and synthetic) are their acidic properties. It is established that the catalyst activity increases with increasing the acidity.

Currently, montmorillonite (MM) - a natural layered aluminosilicate, is being successfully used in matrix of the cracking catalysts in Russia [4]. In addition to participating in formation of porous structure of the catalyst and primary cracking of hydrocarbon molecules of the raw material, MM provides mechanical strength of the catalyst and removal of the heat from the zeolite crystals, helping to preserve its structure and catalytic activity. Modification of MM allows you to optimize its properties for use in the composition of cracking catalysts. In industrial practice, the ion exchange method is used to remove sodium from MM, which negatively affects on activity and stability of the catalyst. Intercalation of MM with oxides of various metals (Al_2O_3, ZrO_2) allows to obtain microporous materials with comparable in structure and acidity of zeolites [5]. It is possible to use methods of influencing the dispersion of MM, for example, ultrasonic processing, since dispersity of the components is important for the formation of porous structure of the catalyst and its mechanical properties [6]. Since indirect indicator of the sorption and catalytic activity of the minerals is value of their exchange capacity, not only the clay minerals, montmorillonite, hydromica, kaolinite and others can be catalysts for the process of organic matter conversion. Clay is a binder in the production of zeolite catalysts, which have found wide application in petrochemistry and oil refining. In addition to improving the strength properties of the catalyst during its transportation and operation, clays also affect chemistry of the processes [7]. By changing amount and composition of the clay binder, you can directly influence selectivity of the contact. It was established that zeolite Y synthesized from kaolin with modulus 4.9 after exchanging 60% Na^+ for H* in it has a high catalytic activity in the reaction of oligomerization of α-octene [8].

Kazakhstan has sufficient reserves of bentonite clays [9], which are widely developed in Kazakhstan. The greatest practical interests are the fields of Southern and Eastern Kazakhstan. In South Kazakhstan, these are the Darbazin and Kelesk deposits with total reserves of 58 million tons, as well as the Andreev, Dzerzhin, Ildersay with total reserves of more than 100 million tons. In East Kazakhstan, the Manrak group of bentonite clay deposits is known with a total estimated resource of about 50 million tons. The high quality of bentonite is allocated Tagan (10.6 million tons) and Dinosaur (about 4 million tons) deposits [10]. Of particular importance is the use of bentonite clays and synthetic zeolites as contacts and carriers for various processes, since they are characterized by a developed surface, porosity and high adsorption capacity.

Kaolinite - a clay mineral from the group of aqueous aluminum silicates. The chemical composition of $Al_4[Si_4O_{10}] (OH)_8$ contains 39.5% Al_2O_3, 46.5% SiO_2 and 14% H_2O. Kaolinite is a widespread clay mineral, the composition of aqueous aluminosilicate (monoclinic), has a layered structure, in nature it occurs in the form of hexagonal or irregular-shaped scales about 1 micron in size. The crystalline structure of kaolinite is based on infinite sheets of $Si – O_4$ tetrahedral having three common oxygen and connected in pairs through free tops with aluminum and hydroxide [11]. Syntheses of highly dispersed and granulated zeolite types of LTA and FAU without binders, which are based on crystallization of metakaolin in solutions of sodium hydroxide and sodium silicate, respectively, have been developed [12, 13].

Modification of layered silicates with a rigid structural cell, which kaolinites are attributed due to the strong hydrogen bonding of individual layers of kaolinite to each other, makes it possible to synthesize a new generation of three-dimensional microporous structures with high specific surface (up to 240 m^2/g) and a significant increase in acid sites due to surface silanol groups [14]. The introduction of catalytically active metals (Pt, Pd, Ni) into the layered structure silicates are leads to the formation of redox centers on the surface, which allows them to act simultaneously as acid and oxidative catalysts [15,16]. Studies conducted previously at the Institute of Organic Catalysis and Electrochemistry named after D.V. Sokolsky using Tagan montmorillonite, which pillared with aluminum and zirconium, showed perspective use of layered clays in the processes of hydrocarbon conversion [17-19]. Previously, with the use of XRD, IR spectroscopy, EPR, we studied the physicochemical properties of Ermak layered kaolinites (KE) and Sarymsak (KS) deposits of Kazakhstan [20]. It has been established that the studied clays along with kaolinite contain montmorillonite, quartz, cristobalite and muscovite impurities. The pore size in the original kaolinites varies between 12-60Å, and most of them are mesopores. Acid treatment of KE and KS contributes to the expansion of the area of mesopores and the growth of their number.

The purpose of this report is to create isomerization catalysts for light n-alkanes based on the modified Ti and Zr natural kaolinites of the Ermak and Sarymsak deposits to produce environmentally friendly high-octane additives to motor fuels.

Experimental part

Methods have been developed for modifying the activated forms of the Sarymsak and Ermak kaolinites (HKS and HKE) with Zr^{4+}, Ti^{4+} cations using $ZrOCl_2$ and $TiCl_4$.

Modified kaolinites of the Sarymsak and Ermak deposits were studied by elemental and X-ray phase analysis (XRF), BET, electron microscopy. Elemental analysis of the samples was performed using an electronic micro analyzer Superprobe 733, Geol (Japan). The synthesized modified clays were studied by X-ray diffraction (XRD) using DRON 4 * 0.7 with CoKα radiation. The specific surface area, pore volume, and pore size distribution were determined by the BET method using low-temperature N_2 adsorption at 77 K (ACCUSORB).

Pt (0.35 wt. %) from H_2PtCl_6 was supported onto the modified kaolinites by impregnation method, followed by washing out of chlorine ions, drying and calcining.

The isomerization reaction was carried out in a flow-type installation in a hydrogen atmosphere and temperatures of 250-400 °C, a molar ratio of $H_2:C_6H_{14} = 3.5$, and a space velocity of n-hexane - 0.82 h^{-1}. Liquid products were analyzed by GLC with a Tsvet chromatograph on a 120-m capillary column. The analysis of gas phase was carried out with an LHM chromatograph on an alumina-packed column. The yield of isomers was accepted as activity of the catalysts.

Result and discussions

The elemental and phase composition of initial, activated and modified kaolinite of Pavlodar deposits was determined by XRD method. The main reflexes of the Sarymsak and Ermak kaolinites (KS and KE) are retained when activated by acid and modifying with Zr^{4+} and Ti^{4+}, while the content of alkaline components of clay (Na_2O, K_2O, MgO) decreases, and reflections of the corresponding oxides appear on the diffractograms: ZrO_2; TiO_2 (anatase) (Table 1, Figure 1). The amount of ZrO_2 in Yermak kaolinite after introduction of ZrO_2 is 4.30%, in Sarymsak -2.41%.

The modification of titanium and zirconium oxides by kaolinites of the Sarymsak and Ermak deposits leads to a decrease in the content of not only oxides of alkali and alkaline earth metals, but also oxides of Fe_2O_3, Al_2O_3 and SiO_2. The ratio of SiO_2/Al_2O_3 with the introduction of TiO_2 increases from 4.4 to 4.6 in the case of HKE and from 4.4 to 4.8 for HKS (Table 1). According to the analysis, amount of TiO_2 increases from 0.4 and 0.6% in the initial kaolinite KS and KE to 36.65 and 34.54%, respectively, after treatment with a solution of titanium oxochloride.

Table 1 - Composition of acid-activated and pillared Zr and Ti clays from the Sarymsak and Ermak deposits

Sample	Quantity, wt.%										Σ,%
	Na_2O	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	K_2O	TiO_2	SO_3	ZrO_2	
KS	1.0	2.5	27.0	60.0	0.8	5.0	3.0	0.4			
HKS	1.11	1.32	16.36	72.08	0.33	4.48	3.16	1.07			100
Zr(7.5)HKS	1.02	0.98	18.59	68.81	0.26	3.59	3.31	1.04		2.41	100
Ti(7.5)HKS	0.61	0.66	10.16	48.54	0.55	2.91	2.02	34.54	-		100
KE	0.8	3.0	15.0	>60.0	3.0	6.0	1.5	0.6			
HKE	0.60	1.18	16.41	71.91	0.33	5.95	2.39	0.97	0.25		100
Zr(7.5)HKE	0.74	0.94	14.93	70.04	0.18	5.69	2.29	0.89		4.30	100
Ti(7.5)HKE	0.33	0.88	9.96	46.02	1.28	3.23	1.66	36.65	-		100

According to the XRF data, the Sarymsak and Ermak clays are among the kaolinite clays. The clearest reflexes of the original Sarymsak and Ermak clays belong to the phases: α-quartz, montmorillonite, kaolinite, and muscovite (Fig. 1). The main reflexes of kaolinites in these two clays are the same, therefore, Fig. 1 shows the diffraction pattern of Ermak kaolinite, and the XRD of the Sarymsak kaolinite is shown earlier in [20].

Intensity, (o.e.)

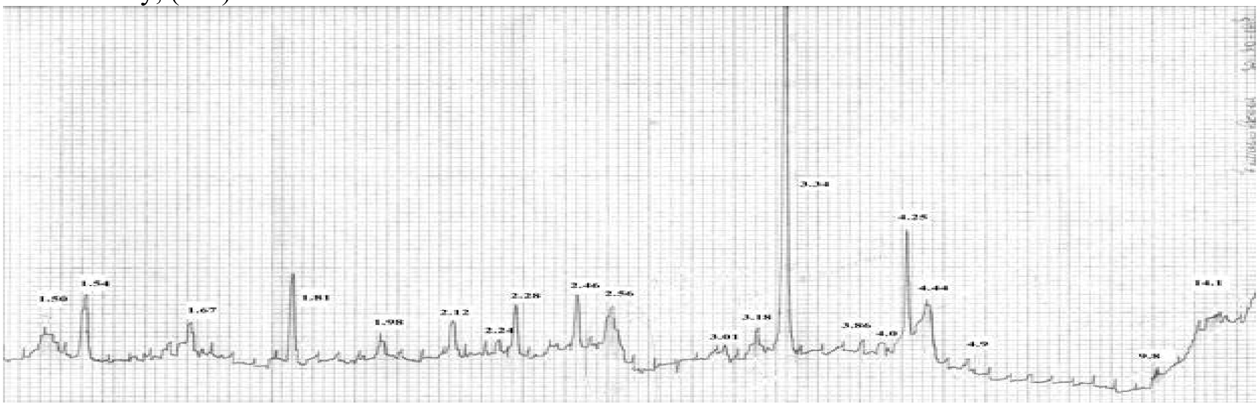

Figure 1 - Diffractogram of the original Ermakov kaolinite (KE)

The defining reflexes in kaolinite are: 7.01-7.02; 3.58-3.60; 3.15-3.18Å. The content of montmorillonite in kaolinites is determined by reflexes: 14.2; 4.44; 1.5Å. The 3.34Å reflex is quartz, and the low-intensity reflexes are 9.80-9.82Å and 4.9Å are the admixtures of muscovite. Acid treatment leads to partial destruction of the structures of kaolinite, muscovite, monorillonite, which is manifested in a decrease in the intensity of reflexes.

The diffractograms of HKE and HKS kaolinites treated with Ti^{4+}, Zr^{4+} ions are almost unchanged compared with the H – form of kaolinite. For illustration, Fig.2 shows the diffractogram of Zr (2.5) HKE.

The main reflexes of KS and KE are preserved when activated by acid and modified with Zr^{4+}, Ti^{4+} ions, while the content of alkaline components of clay (Na_2O, K_2O, CaO) decreases and reflections of the corresponding oxides appear on the diffraction patterns: ZrO_2; TiO_2 (anatase). The appearance of these oxides is also confirmed by the results of elemental analysis (Table 1).

Intensity, (o.e.)

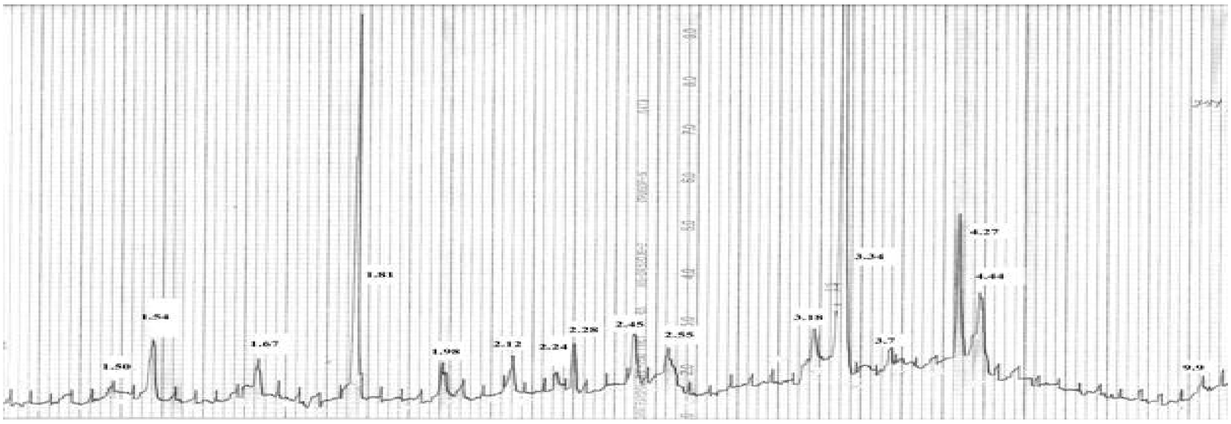

Figure 2 - Diffractogram of modified Zirconium oxide the activated Yermakov kaolinite
Zr (2.5) HKE

Textural characteristics of the Ermak and Sarymsak kaolinites change significantly with the introduction of ZrO_2 and TiO_2 into the composition of kaolinites (Table 2, Figure 3). The total pore volume and average pore diameter increase with transition from initial to the modified samples. The original KS sample is characterized by a relatively wide set of pores with radius of 10–80Å. The maximum number of pores has radius of 40–80 Å, less than 10–30 Å. Acid treatment reduces the number of micropores, while the number of pores with a diameter of 20 - 80 Å increases to 91.6%. In modified Ti^{4+} samples, the effective pore radius are 12.5–50.0 Å. Thus, the modified KS samples are more uniform and more porous than the original clay.

Table 2 - Changes in specific surface area, pore volume, and pore size distribution with an increase the content of Zr and Ti in HKE and HKS

Sample	S, $м^2/г$	Total pore volume, cm^3 / g	Relative content, pores,%	
			Micro -(<20Å)	Mezo -(20-80Å)
KE	92.1	0.287	10.8	89.2
HKE	177.3	0.240	22.8	77.2
Zr(2.5)HKE	135.7	0.147	14.8	85.2
Zr(5.0)HKE	150.9	0.128	37.1	62.9
Zr(7.5)HKE	127.8	0.120	48.5	51.5
Ti (2.5)HKE	150.7	0.298	16.0	84.0
Ti (5.0) NKE	137.4	0.295	19.0	81.0
Ti (7.5) HKE	136.3	0.318	10.0	90.0
KS	49.1	0.119	25.0	74.9
HKS	73.6	0.345	8.4	91.6
Ti (2.5) HKS	123.6	0.203	18.0	82.0
Ti (5.0) HKS	145.0	0.314	7.0	93.0
Ti (7.5) HKS	156.5	0.288	13.0	87.0

Ermak kaolinite has a stable porous structure. Acid treatment and pillaring lead to a slight increase in the specific surface area and proportion of mesopores. Acid activation and modification of Zr leads to a significant increase in the specific surface area of HKE-177.3-127.8 m^2/g (Table 2). The relative content of micropores increases to 48.5% for Zr (7.5) HKE compared to 10.8% for the original kaolinite. The content of mesopores in the modified Zr catalyst decreases from 89.2 to 51.5%.

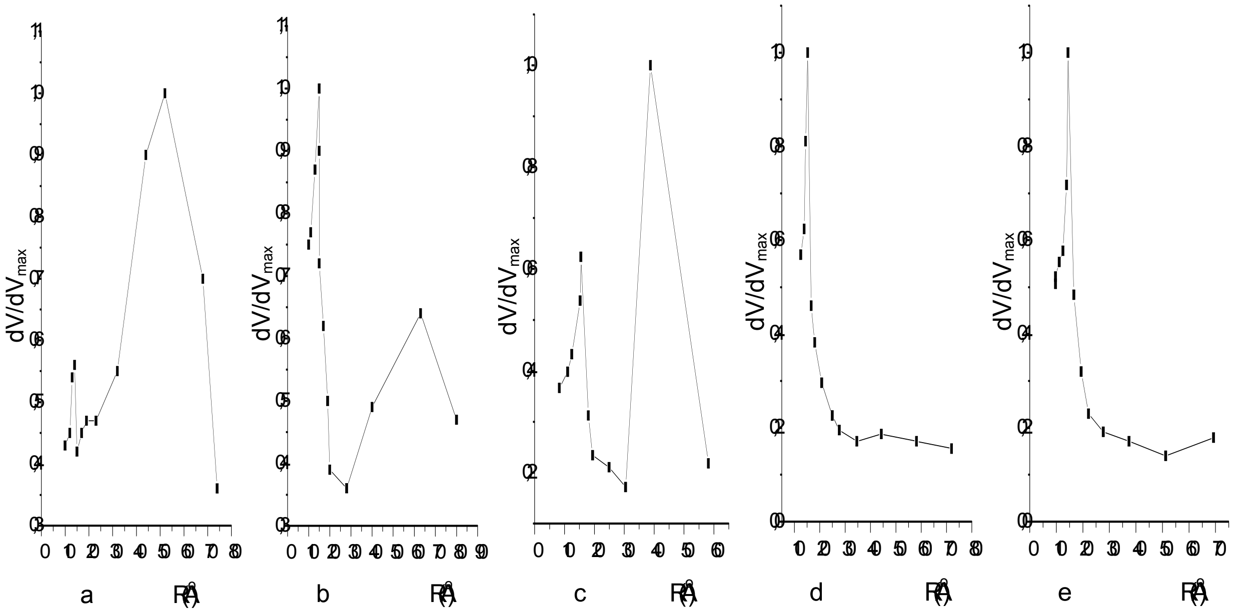

Figure 3 - Pore size distribution in KE kaolinites: a) KE; b) HKE; c) Zr (2.5) HKE; d) Zr (5.0) HKE; e) Zr (7.5) HKE

With introduction of TiO_2 into the composition of kaolinites, a significant change in textural characteristics of the original clays is observed, which is associated with a significant decrease in number of micropores and corresponding increase in number of mesopores as compared results on samples modified with Zr^{4+}.

The isomerizing activity of Pt and Pd catalysts supported on Zr pillared kaolinite from the Yermak field (ZrHKE) are depends on the content of Zr in the carrier and temperature (Table 3). Conversion of n-hexane on the Pt/Zr (2.5) HKE-catalyst is decreases from 18.7 to 15.1% with an increase in temperature from 250 to 400 °C. At this catalyst at all temperatures only C_6, C_7-isomers are formed. The C_6 isomer selectivity decreases with increasing temperature due to the presence of isobutane in the products. With an increase in content of Zr in the HKE to 7.5 mmol/g, the conversion of n-hexane in the temperature range 250-350 °C varies a little, but appeared small amounts of gaseous C_1-C_4 hydrocarbons, which are in the products of disproportionation and hydrocracking reaction.

Table 3 - Isomerization of n-hexane on the Pt-and Pd-catalysts supported on ZrHKE with different zirconium contents

The amount of Zr, mmol / g	T,°C	α,%	S_{C4+}	S_{C6}	Products, wt.%						
					ΣC_1-C_3	Iso-C_4	Iso-C_5	2,2-DMB	2-MPEN	3-MPEN	Iso-C_7
Pt/2.5	250	18.7	100	87.7	-	-	-	-	13.7	2.7	2.3
	300	13.2	100	84.1	-	-	-	-	8.7	2.4	2.1
	350	16.1	100	88.2					11.6	2.6	1.9
	400	15.1	100	77.5		1.3		2.8	5.1	3.8	2.1
Pt/7.5	250	14.2	100	84.5	-	-	-	-	9.5	2.5	2.2
	300	12.4	95.2	68.5	0.6	0.9	0.6	1.6	4.7	2.2	1.8
	350	15	94	55.3	0.9	2.0	1.3	1.5	3.5	3.3	2.5
	400	34.9	94.8	63.3	1.8	3.5	5.2	0.8	16.7	4.6	2.3
Pd/2.5	250	9.0	100	71.1					3.5	2.9	2.6
	300	15.7	100	77.7		0.9			9.3	2.9	2.6
	350	15.4	94.2	57.8	0.9	1.4	1.4	1.6	4.1	3.2	2.8
	400	22.2	95.5	69.4	1.0	1.6	2.4	1.9	8.1	5.4	1.8
Pd/7.5	250	10.5	100	81.0					6.0	2.5	2.0
	300	12.0	100	70.8		1.3			6.0	2.5	2.2
	350	15.4	94.8	62.3	0.8	1.2	1.3	1.4	4.9	3.6	2.2
	400	20.2	88.1	64.5	2.4	0.2	2.9	0.7	7.3	5.0	1.7

The maximum conversion of n-hexane on the Pt/Zr (7.5) HKE was observed at 400° C (34.9%). Under these conditions, the selectivity for C_6 and C_{4+} isomers is 63.3 and 94.8%, respectively. Close patterns of effect of the temperature and Zr content on the isomerization activity are also observed on the Pd/Zr (7.5) HKE catalyst at 400 °C (Table 3).

Tests of Pt and Pd catalysts deposited on Zr pillared kaolinite from the Sarymsak deposit (ZrHKS) showed (Table 4) that the isomerizing activity of these catalysts is significantly higher than Pt and Pd catalysts on ZrHKE (Table 3).

Table 4 - Isomerization of n-hexane on the Pt catalysts supported on ZrHKS with different zirconium contents

Amount of Zr, mmol / g clay	T,°C	α,%	S_{C4+}	S_{C6}	The composition of products, wt.%						
					ΣC_1-C_3	Iso-C_4	Iso-C_5	2.2-DMB	2-MPEN	3-MPEN	Iso-C_7
Pt/2.5	250	14.3	100	88.1	-	-	-	-	10.3	2.3	1.7
	300	7.7	93.5	72.7	0.5	-	-	-	3.5	2.1	1.6
	350	15.2	93.4	57.9	1.0	0.9	2.7	0.5	4.9	3.4	1.8
	400	22.7	95.6	61.7	1.0	1.4	3.0	0.5	8.3	5.2	3.3
Pt/5.0	250	29.0	100	100	-	-	-	-	13.9	15.1	
	300	33.9	100	73.7	-	-	-	-	13.9	11.1	8.9
	350	40.5	100	78.0	-	3.2	-	3.9	7.4	20.3	5.7
	400	43.2	93.3	71.1	2.9	5.2	-	3.1	21.6	6.0	4.4
Pt/7.5	250	9.6	100	78.1	-	-	-	-	5.1	2.4	2.1
	300	8.9	95.5	71.9	0.4	0.4	-	0.4	4.0	2.0	1.7
	350	27.5	94.9	72.7	1.4	3.8	-	1.3	5.3	13.4	2.3
	400	36.9	98.4	70.7	0.6	1.1	4.2	3.4	7.1	15.6	4.9

On the Pt/ZrHKS catalysts with different Zr content, conversion of n-hexane increases with increasing temperature, and the selectivity for C_6 and C_{4+} isomers decreases. The best results on isomerizing activity were obtained on a Pt catalyst supported on ZrHKS with a content of Zr = 5.0 mmol / g. The conversion of n-hexane on this catalyst at 400 °C is 43.2% with a selectivity for isomers of 93.3%, and the yield of isohexanes is 30.7%. It should be noted that on the Pt / Zr (5.0) HKS catalyst in the temperature range 250-350° C, the conversion of n-hexane increases from 29.0% to 40.5% with 100% selectivity for isomers. The gaseous products of n-hexane hydrocracking on this catalyst appear only at 400 ° C. On Pt catalysts deposited on kaolinites with a large (7.5) Zr content, 100% isomer selectivity is observed only at 250° C, and at higher temperatures, the isomer selectivity decreases due to the appearance of gaseous hydrocarbons in the reaction products.

Regularities of effect of the temperature and amount of zirconium modified kaolinite HKS on speed and direction of the process of isomerization of n-hexane on Pd / ZrHKS catalysts (Table 5) are close to those found on Pt / ZrHKS catalysts (Table 4), but selectivity of overall isomers and isohexanes are significantly higher on Pd catalysts compared to results on Pt catalysts. The maximum yield of isohexanes, equal to 31%, was also obtained on a Pd catalyst supported on Zr (5.0) HKS, at 400 °C. The conversion of n-hexane on this catalyst is ~ 5% lower than on the Pt catalyst, however, the yield of isohexanes is slightly higher, due to the higher isomer selectivity. The yield of gaseous C_1-C_3-hydrocarbons on the Pd-catalyst is reduced to 0.5% compared with 2.9% in the same conditions on the Pt-catalyst (Table 4). On a Pd catalyst supported on Zr (7.5) HKS, the conversion of n-hexane varies from 8.3-20.1% depending on the temperature, while the selectivity for all isomers is 100%, and as a result of the reaction mainly 2- and 3-methylpentanes and small amounts (1.5-2.3%) of isoheptanes are formed.

Catalysts based on activated titanium-modified kaolin clay were also tested in the isomerization of n-hexane at various temperatures. For this purpose, catalysts with the composition of 0.35% Pt/Ti (2.5) HKE, Pt/Ti (2.5) HKS, Pd/Ti (2.5) HKE, Pd/Ti (2.5) HKS were prepared. Data on the activity and composition of products resulting from the hydroconversion of n-hexane on Pt- and Pd/Ti HKE catalysts are presented in Table 6 and Fig. 4 and 5.

Table 5 - Isomerization of n-hexane on the Pd-catalysts supported on ZrHKS with different zirconium contents

Amount of Zr, mmol / g clay	T, °C	α,%	S_{C4+}	S_{C6}	The composition of products, wt.%						
					ΣC_1-C_3	Iso-C_4	Iso -C_5	2,2-DMB	2-MPEN	3-MPEN	Iso - C_7
Pd/2.5	250	9.8	100	67.3	-	1.3	-	-	4.2	2.4	1.9
	300	10.8	100	85.2	-	-	-	3.2	4.1	1.9	1.6
	350	15.2	93.4	77.6	1.0	0.7	-	2.8	6.9	2.1	1.7
	400	28.6	98.3	78.3	0.5	0.5	2.5	1.8	17.5	3.1	2.7
Pd/5.0	250	12.3	100	90.2	-	-	-	1.3	5.6	4.2	1.2
	300	19.5	100	85.1	-	1.1	-	3.1	8.3	5.2	1.8
	350	32.8	100	88.4	-	1.3	-	4.7	16.5	7.8	2.5
	400	38.3	98.7	80.9	0.5	3.2	1.2	5.6	17.1	8.3	2.4
Pd/7.5	250	10.1	100	79.2	-	-	-	-	5.5	2.5	2.1
	300	8.3	100	78.3	-	-	-	-	4.4	2.1	1.8
	350	20.0	100	92.5	-	-	-	-	16.7	1.8	1.5
	400	20.1	100	86.6	-	0.4	-	-	15.2	2.2	2.3

Table 6 - Isomerization of n-hexane on Pt- and Pd/Ti (2.5) HKE – catalysts

Catalyst	T T°,C, °C	α, %	S_{C4+}, %	S_{C6}, %	The yield of reaction products,%						
					C_1-C_3	Iso-C_4	n-C_5	2,2-DMB	2MP	3MP	Iso- C_7
Pt/Ti(2.5)HKE	250	25.0	99.4	98.1	0.5	0	0.1	-	8.5	10.1	0
	300	21.6	99.3	97.8	0	0	0.1	0.1	8.7	12.3	0.1
	350	13.0	98.6	95.8	0	0	0.2	0.1	10.0	2.3	0.1
	400	10.4	99.7	94.9	0	0	0.1	0.4	8.1	1.4	0.2
Pd/Ti(2.5/HKE	250	25.7	100	85.7	0	0	0	0	18.4	3.6	2.7
	300	15.2	81.8	70.9	0	0	2.7	0	4.2	6.6	1.5
	350	10.5	82.2	52.4	0.6	0.6	1.2	0	3.1	2.4	1.8
	400	15.4	81.5	55.6	0.7	0.7	2.2	0	5.5	3.0	2.0

The n-hexane conversion on Pt/Ti HKE catalyst is decreases with increasing temperature, selectivity to isomers at all temperatures remains high (98.6 - 99.7%). The maximum conversion of n-hexane is observed at 250°C and equal to 25.0 %. At 400°C, the conversion is reduced to 10.4% with selectivity for all isomers of 99.7%. No hydrocracking products were detected on this catalyst in the temperature range of 350-400 °C. The 2- and 3-methylpentanes and small amounts of 2,2-DMB, n-pentane and isoheptanes are formed from n-hexane.

On the catalyst Pd/Ti HKE at 250 °C, the conversion of n-hexane is maintained at 25.7% with a selectivity of 100% for isomers (Table 6). With increasing temperature decrease in the conversion of n-hexane is observed with a simultaneous decrease in selectivity for all isomers and C_6 - isomers (Table 6, Fig. 5). Thus, the selectivity of Pd/TiHKE-catalyst on C_{4+} decreases from 100% at 250 °C to 81.5% at 400 °C, while on the Pt/TiHKE catalyst the selectivity for C_{4+} does not change. A similar pattern was observed on the effect of temperature on the selectivity of Pt and Pd catalysts for isohexanes (S_{C6}). On Pt/TiHKE, the isohexane selectivity decreases from 98.1% at 250 °C to 95.0% at 400 °C, while on Pd/TiHKE, the isomer selectivity decreases from 85.7% at 250 °C to 55.6% at 400 °C (fig. 4 and 5). Isohexanes, small amounts of isoheptane (2,4-dimethylpentane), n-pentane were detected in the reaction products, and gaseous C_1-C_3 - hydrocarbons appeared at 350 and 400 °C. The absence of a hydrocracking process at temperatures of 300–400 °C is noted for the Pt / TiHKE catalyst.

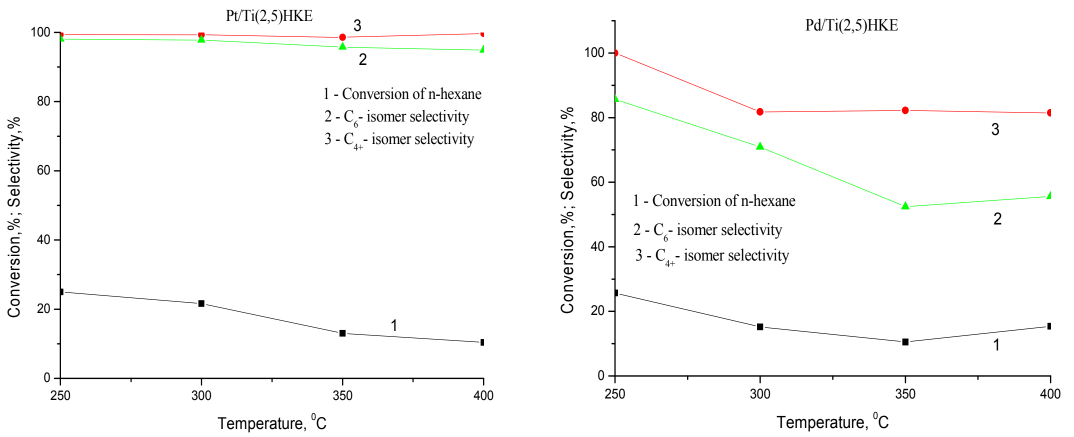

Figure 4 - Conversion of n-hexane and the selectivity of C_6 and C_{4+} - isomers on the catalysts Pt/TiHKE and Pd/TiHKE at different temperatures

In Table 7 presents the data on isomerization of n-hexane on composite catalysts (Pt/Ti/HKS and Pd/Ti/ HKS) based on kaolinite from Sarymsak clay at different temperatures.

Table 7 - Isomerization of n-hexane on Pt- and Pd/Ti (2.5) HKS – catalysts

Catalyst	$T,^0C$	α, %	S_{C4+}, %	S_{C6}, %	The yield of reaction products, %						
					C_1-C_3	Изо-C_4	н-C_5	2.2-DMB	2MP	3MP	Iso-C_7
Pt/Ti(2.5)/HKS	250	9.5	96.1	79.2	0	0	0.4	0	5.3	2.2	2.4
	300	11.1	87.0	50.4	0.5	1.0	0.9	0	3.3	2.3	2.7
	350	22.2	89.5	47.3	0.7	2.7	1.6	0	6.6	3.8	5,2
	400	37.1	86.5	40.6	2.4	4.2	2.5	0.4	9.3	5.7	8.4
Pd/Ti(2.5)/HKS	250	15.3	100	89.0	0	0	0	0	11.2	2.4	1.7
	300	8.9	100	84.4	0	0	0	0	6.5	1.8	1.5
	350	8.4	78.1	53.3	0.4	0.5	1.0	0	2.6	1.9	1.6
	400	17.5	84.6	68	0.5	0.5	1.5	0.7	4.0	7.0	1.7

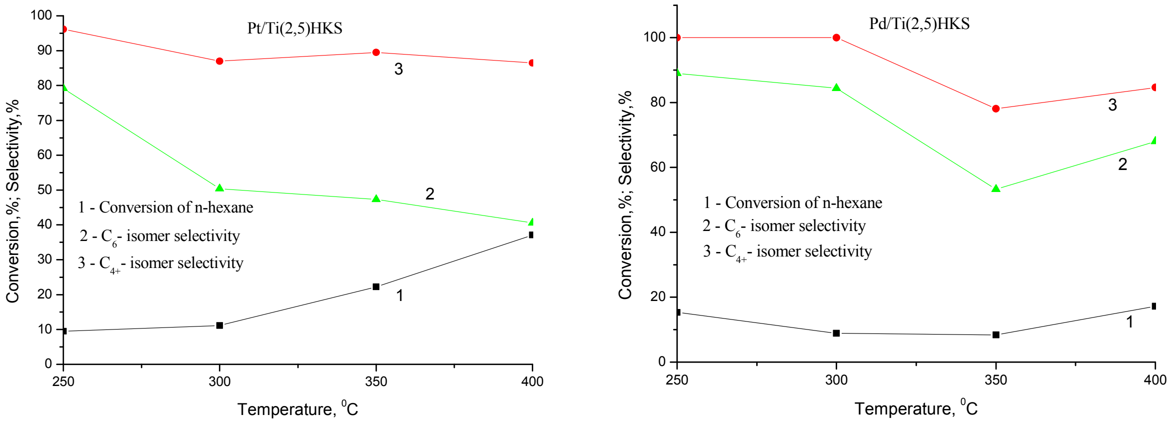

Figure 5 - Conversion of n-hexane and the selectivity of C_6 and C_{4+} - isomers on the catalysts Pt/TiHKS and Pd/TiHKS at different temperatures

From the analysis of the results (Table 7 and Figure 5) it can be seen that the degree of conversion of n-hexane on the Pt/Ti/HKS - catalyst increases from 9.5 to 37.1% with increasing temperature from 250 to 400 °C. The maximum conversion of n-hexane equal to 37.1%, was observed at 400 °C. In contrast to the catalyst on Ermak clay with Pt / TiHKS, increasing temperature, the selectivity for all isomers and for isohexanes is significantly reduced (Fig. 5). At this catalyst, at elevated temperatures (300 and 400 °C), significant amounts of hydrocracking products are formed (Table 7): C_1-C_3 - hydrocarbons (0.5 and 2.4%); isobutane (1.0 and 4.2%); n-pentane (0.9 and 2.5%). In addition to isohexanes, in the reaction products were found isoheptanes: 2,4-DMP (4.0 and 6.0%) and 3,3-DMP (1.2 and 2.4%) at 350 and 400 °C.

The conversion of n-hexane on the Pd/Ti/HKS catalyst is significantly lower than over the Pt/TiHKS (Table 7, Figure 5). High selectivity for isomers is maintained only at 250 and 300 °C, and with increasing temperature, the selectivity for all isomers and isohexanes decreases. Unlike the Pt/Ti HKS catalyst, the amount of hydrocracking products formed at 350-400 °C is significantly lower on the Pd/TiHKS catalyst (Table 7). The amount of isoheptanes formed in the process of hydroconversion of n-hexane on Pd /TiHKS is also lower than over the Pt/Ti/HKS catalyst.

Thus, on the basis of studies performed, it can be concluded that the Pt and Pd catalysts supported on zirconium or titanium modified activated kaolinite exhibit high isomerization activity.

Analysis of results of the n-hexane isomerization on metal catalysts deposited on pillared clays showed that the studied catalysts are distinguished by high selectivity for isomers and insignificant yield of hydrocracking products only at temperatures of 350 and 400 °C. Two of Pt/TiHKE and Pd/TiHKE catalysts showed high activity (conversion of 25.0 and 25.7%) and selectivity (99.4 and 100%) in the isomerization of n-hexane at 250° C.

To reduce the conversion of n-hexane (in parentheses) at 400 °C, the studied Pt and Pd catalysts on modified kaolinites can be arranged in a row: Pt / Zr (5.0) HKS (43.2%)> Pd / Zr (5.0) HKS (38.3%)> Pt / TiHKS (37.1%)> Pt / Zr (7.5) HKE (34.9%). The yield of C6 + C7 isomers in this series of catalysts decreases in sequence: 36% –33.4% –23.9% –24.4%.

The isomer selectivity for the listed catalysts ranges from 93.3-98.7%. The maximum conversion of n-hexane is equal to 43.2% with an isomer selectivity of 93.3%, was observed on 0.35% Pt/Zr (5.0) HKS catalyst at 400° C, which can be recommended for further improvement of process in isomerization of light n-alkanes with obtaining high-octane additives to motor fuel.

Comparison of isomerization results of the n-hexane on metal-supported catalysts showed that the Pt catalysts deposited on modified Zr^{4+} and Ti^{4+} kaolinite is exhibit higher isomerization activity compared to Pd.

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Қ-ГЕКСАНДЫ ИЗОМЕРЛЕНУ РЕАКЦИЯСЫНДАҒЫ ТҮРЛЕНДІРІЛГЕН КАОЛИНИТТЕРДІҢ Pt- ЖӘНЕ Pd-КАТАЛИЗАТОРЛАРЫ

Аннотация. Мақалада екі Қазақстандық – Сарымсақ және Ермаковский кен орындарының Ti^{4+} және Zr^{4+} түрлендірілген каолиниттеріне енгізілген Pt- мен Pd- катализаторларының синтезделуі және қасиеттері бойынша мәліметтері, олардың катализатор құрамы мен температураға тәуелді қ-гексан изомеризациясындағы каталитикалық белсенділіктері көрсетілген. Синтезделген катализаторлардың элементтік және фазалық құрамы, сондай-ақ текстуралық қасиеттері анықталды. Қ-гександы изомерлеу реакциясында зерттелген катализаторлар моно- және қосорынбасарлы изогександар мен изогептандардың пайда болуы нәтижесінде жоғары белсенділік пен селективтілік көрсетті. Ti^{4+} және Zr^{4+} түрлендірілген каолиниттеріне енгізілген Pt-катализаторлары Pd-катализаторларына қарағанда жоғарырақ белсенділік танытты. 400°C кезінде 0.35%Pt/Zr(5.0)HKS –катализаторында өлшемдері бойынша селективтілігі 93.3% болғанда C_6+C_7-изомерлер шығымы 36,0% және қ-гексанның максималды конверсиясы 43.2% болды.

Түйін сөздер: каолинит, платина, палладий, қ-гексан, изомерлеу, селективтілік, изомерлер шығымы, моно- және қосорынбасарлы изогександар.
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Pt- И Pd-КАТАЛИЗАТОРЫ НА МОДИФИЦИРОВАННЫХ КАОЛИНИТАХ В РЕАКЦИИ ИЗОМЕРИЗАЦИИ Н-ГЕКСАНА

Аннотация. В статье представлены данные по синтезу и свойствам Pt- и Pd- катализаторов, нанесенных на модифицированные Ti^{4+} и Zr^{4+} каолиниты двух Казахстанских месторождений - Сарымсакском и Ермаковском (KS, KE), их каталитической активности в изомеризации н-гексана в зависимости от температуры и состава катализатора. Определен элементный и фазовый состав синтезированных катализаторов, а также их текстурные свойства. Показано, что изученные катализаторы проявили высокую активность и селективность в реакции изомеризации н-гексана с образованием моно- и дизамещенных изогексанов и изогептанов. Более высокую изомеризующую активность проявляют Pt-катализаторы, нанесенные на модифицированный Zr^{4+} и Ti^{4+} каолинит по сравнению с Pd. Максимальная конверсия н-гексана, равная 43,2% и выходом C_6+C_7-изомеров 36,0% при селективности по изомерам, равной 93,3%, наблюдалась на 0,35%Pt/ Zr(5.0)HKS -катализаторе при 400°C.

Ключевые слова: каолинит, платина, палладий, н-гексан, изомеризация, селективность, выход изомеров, моно- и дизамещенные изогексаны.

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