ABSTRACT

of the thesis submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D073900 - Petrochemistry
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Nanodispersed Pd-catalysts on acid-activated and pillared aluminum zirconium montmorilonite in the isomerization reaction of light n-alkanes of oil

Research relevance

Due to the strengthening of the requirements of the Technical Regulations of the Customs Union to the quality of motor gasoline fuel, a need arises to replace a larger share of aromatic compounds with products of the isomerization process of hydrocarbons of the pentane-hexane series.

Isomerization of normal alkanes takes a significant place in modern oil refining. Branched alkanes have high octane numbers and are widely used components of environmentally friendly motor fuels. The main method to produce isoalkanes is the skeletal isomerization of n-alkanes on bifunctional catalysts.

One of the promising areas in the synthesis of metal-supported isomerization catalysts is the use of layered aluminosilicates and their modified forms associated with the synthesis of so-called pillared materials characterized by a unique layered-columnar structure as supports, and the use of metal sols as a source of active metal for the synthesis of nanodispersed isomerization catalysts.

Thus, the development of effective isomerization catalysts is a crucial task for the oil refining industry.

Purposes and objectives of the research

The purpose of this research work is to develop new nanodispersed palladium catalysts on supports made of montmorillonite (MM) activated and pillared with aluminum-zirconium for the process of isomerization of n-alkanes, light naphtha of oil into high-octane isomers. To achieve the purposes set, the following objectives have been identified:

1. Synthesis of palladium sols with a certain size of metal particles for their use in the preparation of new nanodispersed palladium catalysts for n-alkane isomerization.

2. Synthesis of activated forms of montmorillonites used as supports and preparation of new nanodispersed palladium catalysts for n-alkanes isomerization from solutions of $PdCl_2$ and Pd-sols on CaHMM and NaHMM.

3. Synthesis of supports from montmorillonite pillared with aluminum-zirconium in Ca- and Na-forms and preparation of new nanodispersed palladium catalysts for isomerization of n-alkanes on these supports from solutions of $PdCl_2$ and Pd-sols.

4. Determination of the physicochemical characteristics of the prepared catalysts: dispersion of metal particles in sols and in supported catalysts based on $PdCl_2$ and Pd-sols, X-ray phase analysis, textural properties, elemental constituents, distribution of acid sites by strength.

5. Testing of synthesized catalysts in n-hexane isomerization and selection of optimal catalyst compositions and process conditions.

6. Testing of the synthesized catalysts in the isomerization of the light fraction of straight-run gasoline to increase the octane number with a complete analysis of the hydrocarbon composition of the feedstock and isomerate.

The scientific novelty of the thesis lies in the fact that there are for the first time

- synthesizing of Pd-catalysts supported on activated CaHMM and NaHMM from solutions of $PdCl_2$ and Pd-sols, determining their elemental and phase compositions, textural and acid characteristics, as well as catalytic activity in the reaction of n-hexane isomerization.
- preparation of the new nanodispersed Pd catalysts, supported on pillared AlZr-montmorillonites in Na- and Ca-forms from solutions of $PdCl_2$ and Pd-sols, determining their textural and acid characteristics, elemental and phase compositions, as well as catalytic activity in the reaction of n-hexane isomerization.
- it has been shown that the studied Pd catalysts are characterized by the prevalence of moderate acid sites and a mesoporous structure, which ensures their high isomerizing activity.
- it has been found that the size of Pd particles on the activated MM ranges from 5-10 nm to 15-20 nm and more, regardless of the exchangeable form of MM. The introduction of mordenite promotes the partial destruction of aggregates of metal particles and a decrease in their number, as well as more uniform distribution of particles over the surface of the support; however, the size of the particles and their aggregates changes little.
- the method of high-resolution transmission electron microscopy has showed that the size of palladium particles in sols, equal to 3.5-5.5 nm, is retained when applied to a support.
- a correlation has been found between the isomerizing activity and the number of moderate acid sites on Pd catalysts from $PdCl_2$ solutions and from Pd sols supported on various supports based on activated and AlZr-pillared MM in Ca- and Na-forms.
- the optimal compositions of nanodispersed Pd-catalysts and conditions for carrying out the process of n-hexane isomerization have been developed, providing the maximum yield of dimethylbutanes and the total amount of mono- and dimethyl-substituted C_6-isomers, equal to 26.0-26.3% and 46.0-47.0%, respectively, with selectivity for C_{4+} isomers (98.3-98.8%) and trace amounts of hydrocracking products.

Scientific ideas submitted for defense:

- determination of the regularities for the formation of the structure of zeolite-free and mordenite-containing Pd-catalysts supported on activated and AlZr-pillared MM in Na- and Ca-forms from solutions of $PdCl_2$ and Pd-sols, by methods of X-ray fluorescence spectroscopy, XRF, BET surface area, TEM, HRTEM, TPD of ammonia.

- results of determining the isomerizing activity of Pd-catalysts in the reaction of n-hexane isomerization depending on the nature of the support, its textural properties, the active metal precursor and its amount, temperature and acidic properties of the catalyst.
- development of optimal compositions of nanodispersed Pd-catalysts and conditions for carrying out the process of n-hexane isomerization, providing the yield of dimethylbutanes and the total amount of mono- and dimethyl-substituted C_6-isomers equal to 26.0-26.3% and 46.0-47.0%, respectively, with isomer selectivity of at least 98%.
- determination of the interrelation between the isomerizing activity of Pd-catalysts of various compositions, prepared from $PdCl_2$ and Pd-sols, with the nature and strength of acid sites.
- Results of isomerization of the light naphtha of straight-run gasoline (IBP - 70°C) on nanodispersed Pd-catalysts in the temperature range 250-400°C, allowing to increase the octane number of gasoline by 20.6 units.

Practical Relevance

Optimal compositions of nanodispersed Pd-catalysts and conditions for carrying out the process of n-hexane isomerization have been developed, providing the maximum yield of dimethylbutanes and the total amount of mono- and dimethyl-substituted C_6-isomers, equal to 26.0-26.3% and 46.0-47.0%, respectively, with selectivity for C_{4+} isomers (98.3-98.8%). These catalysts may be recommended for practical use in the process of isomerization of light naphtha in order to replace zeolite-containing catalysts. The compositions of the optimal catalysts for n-hexane isomerization are protected by 2 utility model patents.

Research work approval. The research results and the main provisions of the thesis were presented at the following scientific conferences: II All-Russian Scientific Conference with international participation “Actual problems of adsorption and catalysis” (Ivanovo, 2017), XII International Conference of Postdoctoral Researchers in Petrochemistry (Zvenigorod, 2018), 25th International Symposium on Metastable, Amorphous and Nanostructured Materials “ISMANAM-2018” (Roma, 2018), 6th International Congress on Microscopy & Spectroscopy “INTERM 2019” (Turkey, 2019).

Publications. According to the results of the thesis, 12 papers were published, of which

- 3 articles in journals recommended by the Committee for Control of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- 2 articles in scientific publications included in the Scopus database, with a non-zero impact factor, as well as in the journal indexed in the Web of Science database;
- 1 article in a foreign journal;
- 4 theses in the materials of international and foreign scientific conferences,

- 2 utility model patents of the Republic of Kazakhstan:

1) Utility Model Patent. N-hexane isomerization catalyst. No. 2978. Publ. Bull. No. 27, dated July 23, 2018. N.A. Zakarina, L.S. Dzhumabayeva.

2) Utility Model Patent. Nanodispersed catalyst for n-hexane isomerization. No. 3497. Bull. No. 48, dated December 21, 2018 N.A. Zakarina, L.S. Dzhumabayeva.

The structure and scope of the thesis. The thesis consists of an introduction, 3 chapters, conclusion, summary and references. The total scope of the thesis is 128 pages, including 59 figures and 38 tables. The references consist of 161 titles of domestic and foreign authors and 2 annexes.

MAIN CONTENTS OF THE RESEARCH

The introduction reflects the importance of this area, shows the relevance of the research and the reasonability of the topic choice, formulates the purposes and objectives of the research, and also shows the scientific novelty and practical significance.

1 Review of literature

The section of the literature review presents the mechanism of catalytic isomerization of n-alkanes and provides a comparative analysis of industrial catalysts for isomerization. The structure and properties of montmorillonites, their use in catalysis, in particular, their use as a support for the preparation of isomerization catalysts are considered. The types of modification of montmorillonite such as acid activation and pillaring are considered. The advantages of nanodispersed particles in heterogeneous catalysis are defined.

2 Experimental procedure

In the experimental part of the research, a diagram of a flow-through unit for n-hexane isomerization is given and the experimental conditions are presented (250-400^{0}C, ʋ=1.0 ml/min, P_{H2}=1 atm). The synthesis of isomerization catalysts is described; the activation procedure and the pillaring technique with aluminum-zirconium systems of Tagansky montmorillonite in Ca- and Na-forms are presented. A procedure for the preparation of palladium sols is described. Methods of physicochemical studies of synthesized catalysts are presented.

3 Results and discussion

This section presents the results of physicochemical studies and the results of n-hexane isomerization on synthesized catalysts.

3.1 Pd catalysts supported on activated Tagansky montmorillonite

3.1.1-3.1.4 Physicochemical characteristics of Pd-catalysts supported on activated montmorillonite in Ca- and Na-forms. Isomerization of n-hexane on Pd/CaHMM and Pd/NaHMM catalysts with palladium content of 0.1 and 0.35%.

Table 1 shows the structural characteristics of MM before and after acid activation.

Table 1 – Textural properties of the initial and activated montmorillonite of Ca- and Na-forms

Sample	S, m^2/g	Total pore volume, cm^3/g	R, Å	Percentage, %	
				Micropores, (0-20Å)	Mesopores,(20-80Å)
CaMM	89,2	0,075	12,0-70,0	46,1	53,9
CaHMM	99,2	0,086	12,5-70,0	40,7	59,3
NaMM	48,2	0,478	12,0-60,0	17,0	83,0
NaHMM	245,1	0,468	15,0-80,0	12,9	87,1

It was shown by the BET method for low-temperature nitrogen adsorption that acid activation leads to an increase in the specific surface area of MM, for the Ca-form of MM, the surface grows from 89.2 to 99.2 m^2/g, while on the Na-form, there is a five-fold increase in the specific surface area from 48.2 to 245.1 m^2/g. In addition, acid activation leads to a decrease in the number of micropores and an increase in the number of mesopores, regardless of the exchange form of MM. Comparison of the porous structure of MM in the Ca- and Na-forms shows that the Ca-form is microporous, while the Na-form is primarily mesoporous, which has a positive effect on the isomerizing activity of the catalyst.

According to the data on the elemental composition of the initial and activated H-form of Tagansky montmorillonite, acid activation leads to the removal of sodium from MM and to a decrease in the content of alkaline components.

According to the XRF data, the montmorillonite structure is not destroyed after activation and thermal calcination.

Transmission electronic microscopy method confirmed the presence of palladium in the Ca-form of MM in the form of a mixture of PdO and Pd_3Si compounds, the sizes of which vary from 5-8 nm to 10-20 nm.

The dispersion of Pd in NaHMM was studied by HRTEM, the particle size varied in the range of 3.5-10.0 nm; at the same time, the studies were carried out in a scanning mode, where the identification of particles was carried out, that are Pd and small amounts of Al and Si.

It is shown that with an increase in temperature from 250 to 400°C, the conversion of n-hexane increases and reaches its maximum value at 400°C (Table 2).

Table 2 - Isomerization of n-hexane on a Pd/CaHMM catalyst at 400°C

Catalyst	α, %	$S_{C6,}$ %	S_{C4+} %	Reaction Product Yield, %					
				{C_1-C_4	i-B	2 MB	2,2 DMB	2MP	ΣC_7
0,1% Pd	32,4	86,0	99,7	0,1	0,2	0,9	16,5	11,3	3,4
0,35%Pd	45,1	81,7	99,6	0,18	0,32	0,69	17,8	15,5	7,0
0,1%Pd+HM	54,3	88,9	99,7	0,16	0,4	0,4	26,0	19,8	5,12
0,35% Pd+HM	54,1	85,7	99,8	0,1	0,2	2,4	25,8	20,6	5,0

During isomerization of n-hexane on Pd-catalysts supported on activated montmorillonite in the Na-form, zeolite-free Pd-catalysts showed the highest catalytic activity (Table 3).

Table 3 – Isomerization of n-hexane on a Pd/NaHMM catalyst at 400°C

Catalyst	α, %	$S_{C6,}$ %	S_{C4+} %	Reaction Product Yield, %						
				Σ(C_1-C_4)	i-B	2 MB	2,2 DMB	2 MP	ΣC_6	ΣC_7
0,1%Pd	52,1	88,3	98,3	0,10	0,25	0,53	26,0	20,03	46,03	5,21
0,35% Pd	54,1	78,9	97,1	0,03	0,50	1,03	23,37	19,28	42,65	9,86
0,1%Pd+HM	47,5	88,4	98,1	0,17	0,28	0,44	23,0	19,0	42,0	4,61
0,35% Pd+HM	43,0	83,2	96,6	0,17	0,32	0,97	18,97	16,8	35,77	5,8

Thus, it was noted that isomerization proceeds well on activated forms of the catalyst in the Ca-form modified with mordenite, and on catalysts supported on the Na-form of MM without the additives of MN zeolite.

3.2 Pd-catalysts supported on AlZr-pillared montmorillonite in n-hexane isomerization reaction

3.2.1-3.2.2 Physicochemical characteristics of Pd-catalysts supported on pillared AlZr-montmorillonite in the Ca-form. Isomerization of n-hexane on Pd/AlZrCaHMM catalysts with a palladium content of 0.1 and 0.35%.

The Table 4 shows the adsorption characteristics of catalysts based on AlZrCaHMM systems supported by palladium chloride.

Table 4 - Specific surface area, effective pore volume and their distribution for Pd/AlZrCaHMM-catalysts

Sample	S,m^2/g	Total pore volume, cm^3/g	R, Å	Percentage, %	
				Micropores, (0-20Å)	Mesopores, (20-80Å)
0,1%Pd/AlZrCaHMM	165,0	0,180	12,5-70,0	57,3	42,7
0,35%Pd/AlZrCaHMM	167,6	0,175	12,5-70,0	46,2	53,8
0,1%Pd/AlZrCaHMM+HM	194,8	0,180	12,0-70,0	50,5	49,5
0,35%Pd/AlZrCaHMM+HM	228,6	0,153	12,0-70,0	54,0	46,0

The maximum amount of mesopores is formed on the 0.35% Pd/AlZrCaHMM and 0.1% Pd/AlZrCaHMM+HM catalysts, on which the maximum value of the n-hexane conversion and the yield of isoproducts are observed.

During hydroisomerization of n-hexane on pillared catalysts with increasing temperature, there is an increase in the conversion of n-hexane with a maximum at temperatures of 350-400°C (Table 5).

Table 5 - Isomerization of n-hexane on a Pd/AlZrCaHMM catalyst

Catalyst	α, %	S_{C6}, %	S_{C6+} %	Reaction Product Yield, %						
				$\{C_1-C_4$	i-B	2-MB	2,2-DMB	2-MP	ΣC_6	ΣC_7
0,1%Pd/AlZrCaHMM	54,4	77,8	91,4	0,4	0,6	3,7	22,4	19,9	42,3	7,4
0,35% Pd AlZrCaHMM	57,9	75,1	91,2	0,4	0,8	3,9	22,7	20,8	43,5	9,3
0,1%Pd AlZrCaHMM +HM	56,9	83,3	90,7	0,9	0,8	3,6	24,5	22,9	47,4	4,2
0,35%PdAlZrCaHMM+HM	55,8	80,0	90,9	1,2	0,5	3,4	22,8	20,7	43,5	7,2

The maximum conversion is observed on a 0.35% Pd catalyst at 400^0C and is 57.9%. The selectivity for C_{6+} isomers on catalysts with different Pd contents remains high enough for all types of catalysts (90.7-91.4%), the selectivity for C_6 is 75.1-83.3%.

3.2.3-3.2.4 Physicochemical characteristics of Pd catalysts supported on pillared montmorillonite AlZrNaHMM. Isomerization of n-hexane on Pd/AlZrNaHMM catalysts with palladium content of 0.1 and 0.35%

The study of texture characteristics showed that the formation of a columnar AlZrNaHMM structure is characterized by an increase in the specific surface area of the samples during pillaring and the introduction of mordenite (Table 6). Catalysts based on AlZrNaHMM have a larger specific surface area, a large pore volume and fewer micropores compared to catalysts based on AlZrCaHMM (Tables 6 and 4).

Table 6 – Structural and adsorption characteristics of Pd catalysts

Sample	S, м^2/г	Total pore volume, cm^3/g	R, Å	Percentage, %	
				Micropores, (0-20Å)	Mesopores, (20-80Å)
0.1%Pd/ AlZr NaHMM	181.5	0.235	10.0-68.0	27.2	72.7
0.35%Pd/AlZrNaHMM	181.8	0.239	10.0-68.0	22.6	77.3
0.1%Pd/ AlZrNaHMM +HM	214.6	0.230	10.0-68.0	30.3	69.7
0.35%Pd/AlZrNaHMM+HM	205.5	0.223	12.0-70.0	28.1	71.8

There is a correlation between the content of the number of mesopores and the activity of 0.35%Pd/AlZrNaHMM-catalyst, on which the maximum conversion of n-hexane is observed, equal to 58.9%, with an isomer selectivity of 91.3% (Table 8).

The Table 7 shows data on the acidity of Pd/AlZrNaHMM catalysts and the effect of mordenite additives on the distribution of a.s.

Table 7 – Acidic properties of Pd/AlZr NaHMM-catalysts (in μmolNH$_3$/g)

Sample	Acid sites			
	Weak <200^{0}C	Medium 200-300^{0}C	Strong > 300^{0}C	Total acidity
0.1% Pd/ AlZr NaHMM	82.5	20.7	0.41	103.71
0.1% Pd/AlZr NaHMM +HM	118.36	73.9	9.29	201.99
0.35% Pd/AlZrNaHMM	80.9	47.4	5.15	133.54
0.35% Pd/ AlZrNaHMM +HM	83.8	44.2	2.35	130.65

The addition of mordenite increases the proportion of medium a.s. on 0,1%Pd-catalyst, which is accompanied by an increase in isomerizing activity, and on 0.35% Pd-catalyst with the addition of mordenite, the content of medium a.s. decreases slightly, which is accompanied by a decrease in isomerizing activity of the catalyst.

The conversion of n-hexane is the highest in the series of Pd/AlZrNaHMM catalyst on a zeolite-free catalyst with a palladium content of 0.35%, which is 58.9%, the yield of iso-C$_6$ is 46%, and iso-C$_7$ is 7.8% (Table 8).

Table 8 - Isomerization of n-hexane on catalysts based on Pd/AlZrNaHMM at 400°C.

Catalyst	α, %	S_{C6}, %	S_{C6+} %	Reaction Product Yield, %		
				2,2-dimethylbutane	2-methylpentane	ΣC_7
0.1%Pd /AlZrNaHMM	50.6	87.0	94.3	24.41	19.63	3.68
0.35%Pd/ AlZrNaHMM	58.9	78.1	91.3	26.0	20.0	7.8
0.1%Pd/AlZrNaHMM+ HM	54.1	85.5	98.2	24.5	19.1	6.9
0.35%Pd/AlZrNaHMM+HM	50.7	87.1	97.9	24.53	19.61	5.50

The addition of mordenite into the Pd/AlZrNaHMM composition increases its activity on a low-percentage catalyst of 0.1%, and on 0.35% Pd, the conversion of n-hexane decreases. The same tendency was observed on the Pd-catalyst on pillared MM in the Ca-form. The selectivity for the formed S_{C6+} isomers remains rather high of 91.3-98.2% for all types of catalysts.

3.3 Pd-sol catalysts supported on activated Tagansky montmorillonite in the reaction of n-hexane isomerization

3.3.1-3.3.4 Physicochemical characteristics of nanodispersed Pd catalysts supported on activated CaHMM and NaHMM montmorillonite.

The textural characteristics of Pd-sol catalysts supported on activated CaHMM and NaHMM montmorillonite were studied. It was found that modification with mordenite leads to an increase in the specific surface area of samples with a Pd content of 0.1% and 0.35%, for Ca- and Na-forms.

For visual clarity, Figure 1 shows changes in the conversion of n-hexane, the yield of isohexanes, and selectivity for isomers on 0.35% Pd-catalyst depending on temperature. As can be seen from the figure, with increasing temperature, there is an increase in conversion and yield of isohexanes, and selectivity for C_{6+} increases.

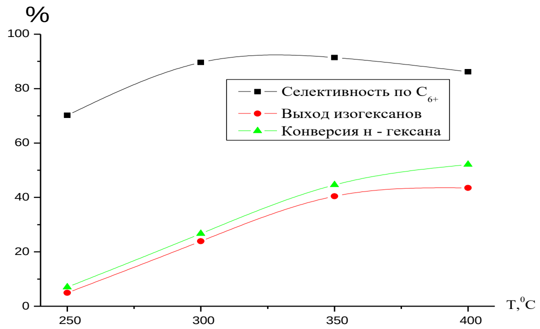


Figure 1 – Yield of isohexanes, selectivity and conversion of n-hexane isomerization process on 0.35% PdZ/CaHMM catalyst, depending on the process temperature

On Pd-sol catalysts supported on activated montmorillonite in the Na-form, there is also an increase in the yield of isohexanes and the yield of C_{4+} with increasing temperature (Fig. 2).

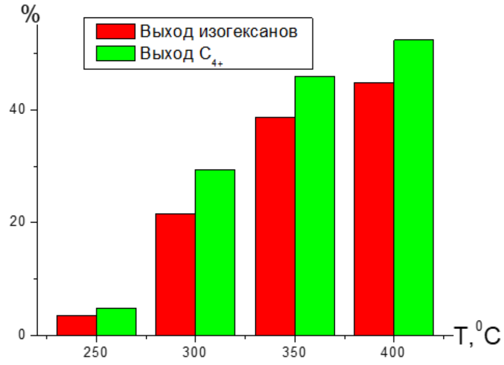


Figure 2 – Temperature dependence of the yield of isohexanes and C_{4+}-isomers on a 0.35% PdZ/NaHMM catalyst

3.4 Pd-sol catalysts supported on AlZr pillared MM in the reaction of n-hexane isomerization

3.4.1-3.4.2 Physicochemical characteristics of nanodispersed Pd catalysts supported on pillared montmorillonite AlZrCaHMM. Isomerization of n-hexane on PdZ/AlZrCaHMM catalysts with a palladium content of 0.1-0.35%

When studying the textural characteristics, it was shown that modification with mordenite leads to an increase in the specific surface area. The dispersion of the active metal particles was determined by the method of transmission electron microscopy; the particle size varies in the range of 3.5-5.5 nm.

The results of the isomerization of n-hexane on the Pd-sol/AlZrCaHMM catalyst at the optimum temperature are presented in Table 9.

Table 9 – Isomerization of n-hexane on a PdZ/AlZrCaHMM catalyst

Catalyst	α, %	S_{C6}, %	S_{C6+} %	Reaction Product Yield, %						
				{C_1-C_4	i-Б	2-MB	2,2 DMB	2 MP	ΣC_6	ΣC_7
0,35%PdZ/AlZrCaHMM(400°C)	56,8	79,1	93,6	0,2	0,5	3,0	25,2	19,8	45	8,17
0,1%PdZ/AlZrCaHMM(400°C)	46,6	82,5	93,8	0,43	0,45	2,0	19,9	18,5	38,4	5,23
0,35%PdZ/AlZrCaHMM+HM(400°C)	57,8	73,9	87,3	0,5	2,5	4,3	23,4	19,3	42,7	7,8
0,1%PdZ/AlZrCaHMM+HM (350°C)	51,8	83,9	90,1	0,34	1,5	3,3	23,7	19,8	43,5	3,23

The conversion of n-hexane increases with an increase in the Pd content and reaches 56.8% on a 0.35% PdZ catalyst with an isohexane yield of 45.0% at 400^0C.

The introduction of mordenite into the composition of 0.35% PdZ / AlZrCaHMM + HM- catalyst increases the activity, and the conversion of n-hexane increases to 57.8%, the yield of isohexanes to 42.7%. Selectivity for C_{6+} isomers is 87.3-93.8%.

3.4.3-3.4.4 Physicochemical characteristics of Pd sol catalysts supported on pillared montmorillonite AlZrNaHMM. Isomerization of n-hexane on PdZ/AlZrNaHMM catalysts with a palladium content of 0.1-0.35%

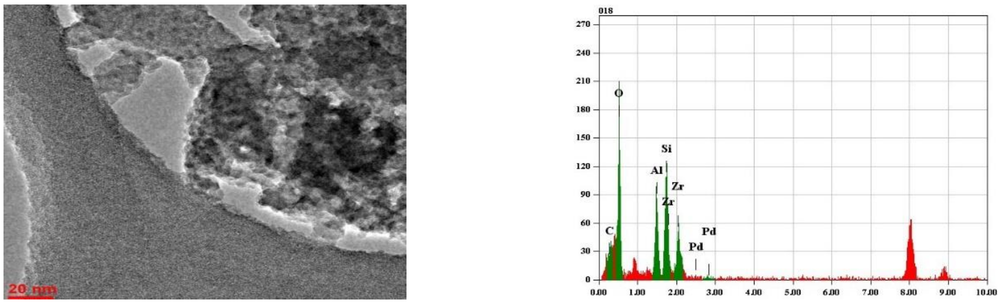
The results of n-hexane isomerization on the studied Pd catalysts at an optimal temperature of 400°C are presented in Table 10.

The maximum conversion of n-hexane was found on 0.35% of the PdZ catalyst, which is 59.5%, the yield of isohexanes reaches 47.0%. The selectivity for C_6+ isomers on catalysts with different Pd contents, as well as those modified with mordenite, remains high enough at 91.7-98.7%.

Table 10 — Activity, selectivity and yield of n-hexane isomerization products on 0.1 and 0.35% PdZ/AlZrNaHMM catalysts

Catalyst	α, %	S_{C6}, %	S_{C6+} %	Reaction Product Yield, % wt.						
				{C_1-C_4	i-B	2MB	2,2DMB	2MP	Σ C_6	ΣC_7
0,35% PdZAlZrNaHMM	59,5	79,0	91,7	0,37	0,82	3,78	26,3	20,7	47,0	7,5
0,1%PdZAlZr NaHMM	47,1	87,4	95,4	-	0,43	1,73	22,2	19,0	41,2	3,8
0,35%PdZAlZrNa HMM+HM	52,6	83,4	97,8	0,06	0,36	0,72	24,3	19,6	43,9	7,6
0,1%PdZAlZr NaHMM+HM	48,1	89,9	96,7	0,18	0,65	0,77	23,8	19,4	43,2	3,3

The dispersion of palladium particles produced when coating on pillared AlZrNaHMM was determined using an electron microscope (HRTEM). Pd nanoparticles are uniformly distributed over the support surface. The size of the palladium particles when coated to a support remains approximately the same as in the initial sol (3.5-5.0 nm). (Figure 3).



a b

Figure 3 - HRTEM images of the Pd-sol/AlZrNaHMM+HM catalyst: a-transmission microscopy (500000 magnification), b - scanning mode

In parallel, studies were carried out in scanning mode with attachment for X-ray energy dispersive microanalysis (EDX analyzer), where the content of Pd, Al and Zr was confirmed.

Based on the results of the data obtained, a comparison was made of the results on the isomerizing activity of $PdCl_2$ and Pd-sol catalysts; it was shown that, in terms of the conversion of n-hexane and the yield of isomers, higher results were obtained on catalysts from palladium sols. 0.35% Pd - sol supported on pillared with aluminum-zirconium montmorillonite in Na- form, without the addition of mordenite, is the most active in the process of n-hexane isomerization (Figure 4).

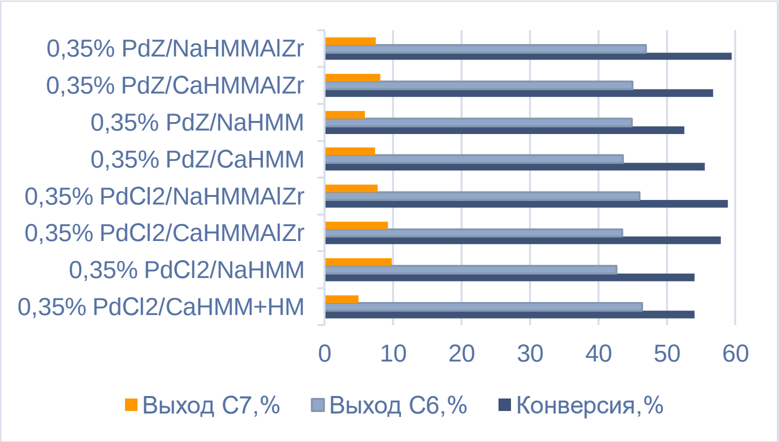


Figure 4 – Conversion, yield of C_6 and C_7 isomers of the most effective catalysts

3.4.5 Isomerization of light naphtha of straight-run gasoline on 0.35%PdZ/AlZrNaHMM catalyst

Since 0.35% Pd-sol/AlZrNaHMM exhibited the highest activity in the isomerization reaction of n-hexane, it seemed appropriate to test this catalyst in the process of isomerization of a light naphtha of straight-run gasoline (IBP - 70°C).

Isomerization of the light naphtha of straight-run gasoline on 0.35% PdZ/AlZrNaHMM catalyst at different temperatures leads to a significant change in the composition of gasoline and an increase in octane numbers.

Tests were carried out with a catalyst volume of 50 ml in the process of isomerization of the light naphtha of straight-run gasoline (IBP - 70°C), it was shown that the increase in the octane number (RON) was 20.6 units, mainly due to isomerization of n-alkanes and their dehydrocyclization.

Thus, the structural characteristics and acidic properties of the catalyst have a determining influence on the activity, selectivity, and yield of isomers; in addition, the state and dispersion of active metal particles, which carry a hydrodehydrogenating function in the isomerization of n-alkanes, have a definite effect on the activity.

The greatest activity in the reaction of n-hexane isomerization was shown by PdZ/AlZrNaHMM, the conversion of which was 59.5% with an isohexane yield of 47.0%.

SUMMARY

1. New Pd catalysts based on activated and AlZr-pillared Tagansky montmorillonite (MM) in Na and Ca-forms have been synthesized using solutions of $PdCl_2$ and Pd-sols obtained by decomposition of palladium polyoxomolybdates, their phase and elemental compositions, textural and acidic characteristics, as well as the dispersion of palladium particles and the composition of particles on the surface of the support have been determined.

2. It has been shown that the activation of MM with acid makes it possible to reduce the amount of alkali and alkaline-earth metals in MM and, thus, to standardize the MM composition in various exchangeable forms, and the stage of MM pillaring promotes an increase in the specific surface area, an increase in the amount of mesopores and an increase in MM acidity.

3. It has been shown that the studied Pd catalysts are characterized by a predominance of acid sites of medium strength and a mesoporous structure, which ensures their high isomerizing activity.

4. The size of Pd particles on the activated MM ranges from 5-10 nm to 15-20 nm and more, regardless of the exchangeable form of MM. The addition of mordenite promotes the destruction of aggregates of metal particles and a decrease in their amount, as well as a more uniform distribution of particles over the surface of the support; however, the size of the particles and their aggregates changes little. The high-resolution transmission electron microscopy method has shown that the size of palladium particles in sols is retained when they are coated on a support.

5. A correlation has been found between the isomerizing activity and the number of medium acid sites on Pd catalysts from $PdCl_2$ solutions and from Pd sols coated on various supports based on activated and AlZr-pillared MM in Ca- and Na-forms.

6. A 0.35% PdZ/AlZrNaHMM catalyst has been tested in a reactor with a catalyst volume of 50 ml in the process of isomerization of a light fraction of straight-run gasoline (IBP - 70°C) with varying temperature and feed space velocity. It is shown that under the optimal conditions of the process, the increase in the octane number (RON) was 20.6 units, mainly due to isomerization of n-alkanes and their dehydrocyclization.

7. Optimal compositions of nanodispersed Pd-catalysts and conditions for carrying out the process of n-hexane isomerization have been developed, providing the maximum yield of dimethylbutanes and the total amount of mono- and dimethyl-substituted C_6-isomers, equal to 26.0-26.3% and 46.0-47.0%, respectively, with selectivity for C_{4+} isomers (98.3-98.8%) and trace amounts of hydrocracking products. These catalysts may be recommended for practical use in the process of isomerization of light naphtha in order to replace zeolite-containing catalysts. The compositions of the optimal catalysts for n-hexane isomerization are protected by 2 utility model patents of the Republic of Kazakhstan.