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Isomerization of N-Hexane on Pd-Catalysts on Pillared Aluminum-Zirconium Montmorillonite

N. ZAKARİNA[a], L. DJUMABAYEVA[a,b*], A. ABİLMAGZHANOV[a]

[a]*D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Kunaev St. 142, 050010,*
Almaty, Republic of Kazakhstan,

[b]*The Kazakh National Research Technical University after K.I. Satpaev,*

Abstract:

Pd-catalysts supported on pillared aluminum-zirconium Tagan (Kazakhstan) montmorillonite (MM) from PdCl2 and Pd-sol were synthesized and their textural, acidic and catalytic properties in the isomerization of n-hexane were investigated, depending on content of the active metal and the temperature. It was shown that the activity and selectivity of Pd catalysts in the isomerization of n-hexane change little with decreasing of palladium content at different temperatures. On a 0.35% Pd-catalyst at 400°C, the content of C6 isomers is 46.0%, with a decrease of the palladium content to 0.1%, the isohexanes yield is 44.0% at a temperature of 350°C. The C6-isomers yield on the Pd-catalyst from sol is 47%, while on Pd it is 46%. A slightly increased isomerization activity of Pd-sol catalysts can be explained by a large number of average acid sites found on this catalyst as compared with the results obtained on the Pd-catalyst from PdCl2. The particle size of palladium in a 0.35% Pd/AlZrNaHMM +HM-catalyst found for two different areas of the catalyst varies from 2.7 to 5.2 nm.

Keywords: Isomerization; N-Hexane; Pillared Montmorillonite; Palladium Catalyst; Acid Site.

DOI:

1. INTRODUCTION

One of the most effective ways to improve the antiknock properties of straight-run gasoline is the catalytic isomerization of n-alkanes resulting in high-octane environmentally friendly isomers [1-5]. In the course of isomerization, the molecular structure of normal paraffins is rearranged into their isomers with a higher octane number. Adding the high-octane isomerized pentane-hexane hydrocarbons and light gasoline fractions ensures an increase in the octane number of environmentally friendly motor fuels with a low benzol content and total aromatics content in commercial gasoline. In this context, the production of highly efficient catalysts for this process, suitable for mild conditions, seems to be a relevant objective.

Pillared clay-based catalysts due to their high acidity and regulated porous structure, wherein mesopores predominate, demonstrate high activity and selectivity during the isomerization of n-paraffins with the formation of mono- and disubstituted isomers [3,4]. Pillarization of Tagan montmorillonite (MM) by the bioxide Al:Zr-system increases stability of Pt- and Pd-based catalysts and facilitates the formation of nano-sized metal catalysts due to the predominant number of mesopores in the pillared Al:Zr montmorillonite in the Ca-form. [3]. High isomerization activity of the Pt- and Pd/AlZrCaHMM-catalysts was demonstrated earlier at 350 and 400^{0}C, which was accompanied by the formation of C_6-C_7 mono- and disubstituted isomers from n-hexane [4].

The object of this paper is to conduct the synthesis of Pd-catalysts deposited on activated AlZr-pillared

Corresponding Author E-mail: djumabaevals@mail.ru

montmorillonite in the Na-form (NaHMM) and to study their textural, acidic and catalytic properties in the isomerization of n-hexane, depending on the quantity of active metal, temperature and mordenite additives (HM).

2. EXPERIMENTAL PROCEDURE

Hydroxocomplexes of aluminum and zirconium were used as fixing agents for the synthesis of pillared aluminum–zirconium MM. These hydroxocomplexes were introduced into interlayers of the montmorillonite using known methods [6-7]. In synthesized samples the Zr^{4+}/ clay and Al^{3+}/ clay ratio was 2.5 mmol/g clay. Textural characteristics of the samples were determined based on the low-temperature adsorption of nitrogen by the BET method using ACCUSORB. The acidity of the catalysts was determined by the thermoprogrammed desorption of ammonia (TPD NH3) using the chemical absorption analyzer USGA-101 (UNISIT).

The dispersion of active metal particles was determined by the high-resolution transmission electron microscopy (HRTEM) using JEM 2100 (JEOL) with a working electron energy of 200 keV.

Phase composition of the catalysts was determined by the X-ray phase analysis using the X-ray diffractometer DRON-4*0.7 with CoKα and CuKα radiation.

The catalysts were tested during the hydroisomerization of the model hydrocarbon — n-hexane. The process took place in the temperature range of 250-400°C, under the atmospheric pressure of hydrogen and at the molar ratio of $H_2:C_6H_{14}=3.5$ and the n-hexane flow rate of 0.82 h^{-1}. The catalyst volume was 5 cm^3. Reaction products were analyzed through the method of gas-liquid chromatography, using the chromatograph 3700 and the capillary column (50 m) filled with squalane.

Palladium (0.35 wt%) and (0.1 wt%) were added to the pillared Al-Zr-montmorillonite by impregnation with a solution of PdCl2 and a solution of Pd-sol which was prepared by the reduction of Pd (II) polyhydroxocomplexes containing polyoxoanions Mo (VI), followed by thermal decomposition (500°C) into oxides and reduction by hydrogen at 450°C.

3. RESULTS and DISCUSSION

Table 1 below shows the textural characteristics of the original NaMM, acid-activated NaHMM, Pd-catalysts supported on pillared Al-Zr-montmorillonite and mordenite-modified (HM) Al:ZrNaHMM. MM activation by a solution of H_2SO_4 increases the specific surface of the sample from 48.2 m^2/g to 245.1 m^2/g. As the BET analysis proved, the formation of the pillared AlZrNaHMM structure is characterized by the increased specific surface of the samples and the increased number of micropores as compared with the original NaMM. Size distribution of pores showed that with the Pd quantity decreasing from 0.35 to 0.1%, the number of mesopores falls from 77.3 to 72.7%, and the number of micropores increases from 22.6 to 27.2%.

Modification of Pd-catalysts by mordenite increases the specific surface and the number of micropores, regardless of Pd content in the catalyst.

The catalytic properties of bifunctional catalysts of n-alkane isomerization are predicated upon the nature and strength of acid sites, depending on the availability of active sites for reacting molecules. As the Table 2 below shows, adding the mordenite increases the share of average acid sites (200 <T <300°C) by 16.6% on the catalyst with a palladium quantity of 0.1%, which is accompanied by the increased isomerizing activity, and the quantity of average acid sites slightly decreases on the 0.35% Pd-catalyst with the addition of mordenite, which is accompanied by the decreased isomerizing activity of the catalyst.

Corresponding Author E-mail: djumabaevals@mail.ru

Table 1. Comparative structural and adsorption characteristics of the original Na-form, activated and pillared H-form of the Tagan montmorillonite and Pd-based catalysts

Sample	S, m^2/g	Total volume of pores,cm^3/g	R, Å	Relative quantity, %, %	
				Micropores, (0-20Å)	Mesopores, (20-80Å)
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
0.1%Pd/Al:Zr NaHMM	181.5	0.235	10.0-68.0	27.2	72.7
0.1%Pd/Al:Zr NaHMM+HM	214.6	0.230	10.0-68.0	30.3	69.7
0.35%PdAl:Zr/ NaHMM	181.8	0.239	10.0-68.0	22.6	77.3
0.35%Pd/Al:Zr NaHMM+HM	205.5	0.223	12.0-70.0	28.1	71.8

Table 2. Acidic properties of zeoliteless and mordenite-modified 0.1 and 0.35% Pd/AlZr NaHM -catalysts

Sample	Quantity of acid sites	Acid sites			
		Weak <200^0C	Average 200-300^0C	Strong > 300^0C	Total Acidity
0.1% Pd/ AlZr NaHMM	%	79.59	20	0.4	100
	µmol NH_3/g	82.5	20.7	0.41	103.71
0.1% Pd/AlZr NaHMM +HM	%	58.6	36.6	4.6	100
	µmol NH_3/g	118.36	73.9	9.29	201.99
0.35% Pd/AlZr NaHMM	%	60.6	35.52	3.86	100
	µmol NH_3/g	80.9	47.4	5.15	133.54
0.35% Pd/ AlZr NaHMM +HM	%	64.15	33.9	1.88	100
	µmol NH_3/g	83.8	44.2	2.35	130.65
0.1% PdZ* /AlZr NaHMM +HM	%	25.0	43.0	31,9	100
	µmol NH_3/g	61.75	106.3	78.9	247
0.35% PdZ* /AlZr NaHMM +HM	%	27.3	42.8	30.60	100
	µmol NH_3/g	69.7	109.2	78.06	255

*PdZ- Palladium sols-based catalyst

Corresponding Author E-mail: djumabaevals@mail.ru

The total number of acid sites is significantly higher in the palladium sols-based catalysts modified by mordenite than in the catalysts obtained by the impregnation with a solution of $PdCl_2$, and the total number of acid sites is growing with an increase of palladium from 0.1 to 0.35%. The quantity of average acid sites on these catalysts is also higher than the quantity of strong ones. Furthermore, the relative number of average acid sites on the Pd sols-based catalysts is 6.4–8.9% higher than on the Pd-catalysts from $PdCl_2$.

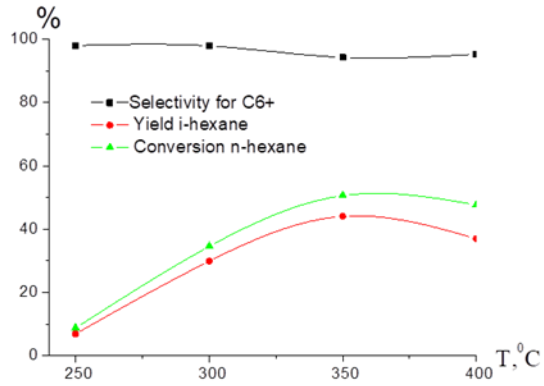
Table 3 shows results of the hydroconversion of n-hexane on the 0.1% and 0.35% Pd/AlZrNaHMM- and α - conversion of n-hexane; S- selectivity to C_6 (SC6) and C_{6+}(SC_{6+}).C_{6+} -hydrocarbons with number of carbon atoms more than 6Pd/AlZrNaHMM+HM- catalysts at different temperatures. The efficiency of the obtained catalysts was evaluated based on the n-hexane conversion, selectivity and yield of C_6 and C_7 - isomers. The highest conversion of n-hexane is achieved at 350-400^{0}C. Selectivity to the resulting isomers SC_{6+} is fairly high 91.3-98.2% at all temperatures. Zeoliteless catalysts demonstrated good results. Maximum yields of isohexanes were obtained on the 0.1% Pd/AlZrNaHMM-catalyst at 350^{0}C and the 0.35% Pd/AlZr HHMM-catalyst at 400^{0}C, which equal to 44.03% and 46.0%, respectively.

Table 3. Isomerization of n-hexane on zeoliteless and mordenite-modified 0.1 and 0.35% Pd/AlZr NaHMM-catalysts

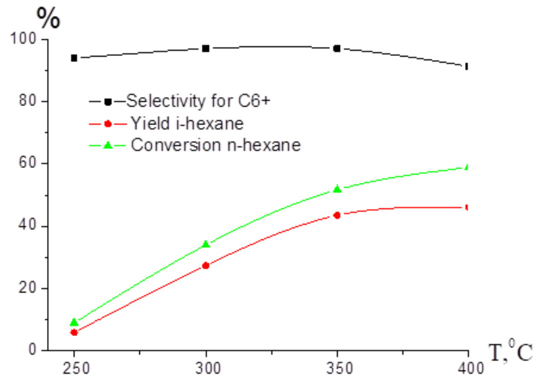
Catalyst	T, ^{0}C	α, %	$S_{C6,}$ %	S_{C6+} %	The yield of reaction products, %		
					2,2-Dimethyl butane	2-Methyl pentane	Amount isoC_7
0.35% Pd	250	9.0	65.6	93.9	3.5	2.5	2.6
	300	34.0	80.6	97.0	15.8	11.6	5.6
	350	51.7	84.3	97.0	24.0	19.6	6.6
	400	58.9	78.1	91.3	26.0	20.0	7.8
0.1% Pd	250	8.7	78.4	98.0	3.97	2.87	1.71
	300	34.5	86.5	97.9	17.17	12.70	3.94
	350	50.6	87.0	94.3	24.41	19.63	3.68
	400	47.6	77.7	95.3	19.96	16.99	8.38
0.35% Pd+ HM	250	14.7	80.6	97.9	7.0	4.85	2.55
	300	37.1	90.7	97.6	19.3	14.32	2.55
	350	43.6	91.9	96.6	22.52	17.53	2.05
	400	50.7	87.1	97.9	24.53	19.61	5.50
0.1% Pd+ HM	250	13.9	83.8	97.8	7.1	4.6	1.9
	300	43.8	91.6	97.6	21.8	18.3	2.7
	350	45.0	90.9	96.3	22.0	17.1	2.4
	400	54.1	85.5	98.2	24.5	19.1	6.9

Corresponding Author E-mail: djumabaevals@mail.ru

The figures below show the activity, selectivity and yield of iso-compounds on Pd-catalysts during the isomerization of n-hexane at different temperatures (Fig. 1).



(a)



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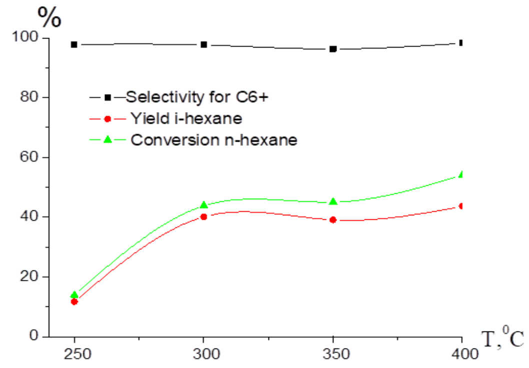

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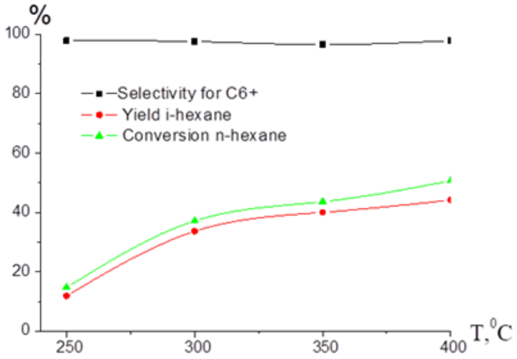


(d)

Figure 1. Isomerization of n-hexane on 0.1%Pd/AlZrNaHMM **(a)**; 0.35%Pd/AlZrNaHMM **(b)**; 0.1%Pd/AlZrNaHMM+HM **(c)**; 0.35%Pd/AlZrNaHMM+HM **(d)** – catalysts depending on the process temperature

The n-hexane conversion increases with temperature and reaches 58.9% on the 0.35% Pd-catalyst at 400^{0}C and 50.6% on the 0.1% Pd-catalyst at 350^{0}C. Selectivity to C6+ isomers remains high (91.3%) at 400^{0}C. On the 0.35% Pd-catalyst at 400^{0}C, the content of C_6-isomers is 46.0%, with a decrease of the palladium content to 0.1%, the isohexanes yield is 44.0% at a temperature of 350°C. When adding the mordenite on the 0.1% Pd-catalyst at 350^{0}C, the yield of C_6-isomers falls by 5%, and increases by 7% at 400^{0}C. On the 0.35% Pd-catalyst, after adding the mordenite the yield of isomers decreases by 1.9 and 3.5% at 350^{0}C and 400^{0}C, respectively.

The yield of isomers positively affects the octane number. Fig. 2 shows the dependence of the octane number of the palladium catalyst-based n-hexane isomerization products on the Pd quantity and mordenite addition.

Corresponding Author E-mail: djumabaevals@mail.ru

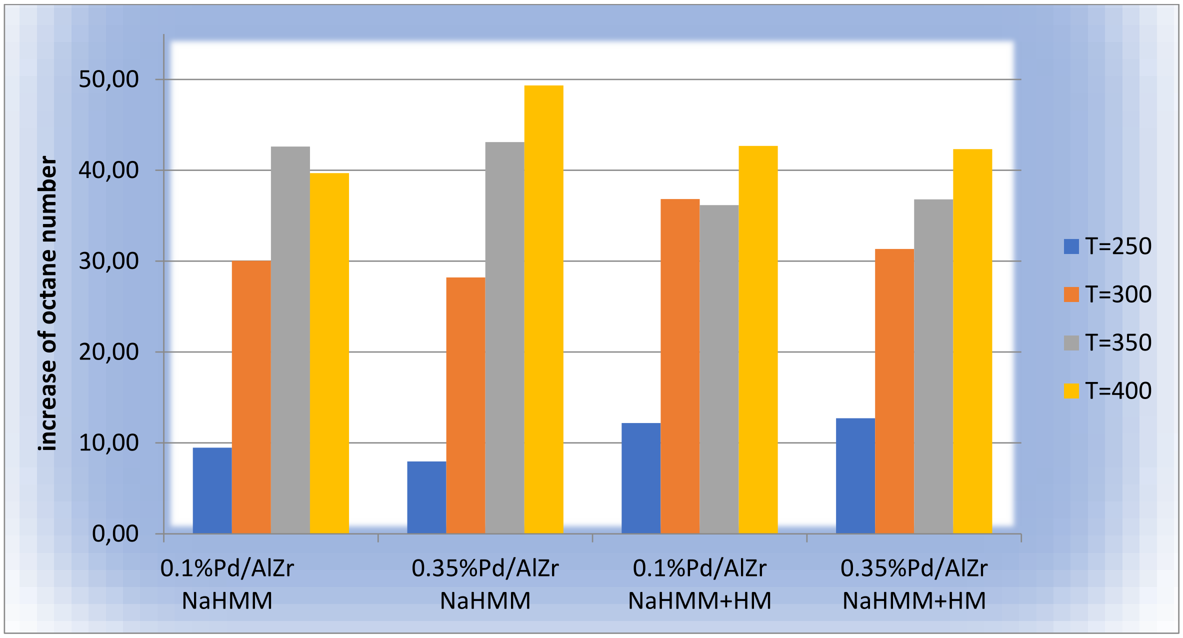


Figure 2. Temperature dependence of the octane number of products obtained from n-hexane isomerization using the studied 0.1% and 0.35% Pd/AlZr NaHMM and Pd/AlZrNaHMM +HM-catalysts.

Fig. 2 shows that the octane number increases with the rising temperature, which is attributed to the increased yields of mono- and disubstituted C_6-C_7-isomers. The maximum increase in the octane number is observed on the 0.35% Pd/AlZr NaHMM-catalyst and equal to 49.4. The mesopore quantity of these catalysts is 69.7-77.3%, which affects the yield of isomerization products (Table 1). The porous structure of the catalysts and the number of acidic sites of a certain strength influence on the direction of the process itself and the yield of isomerization products.

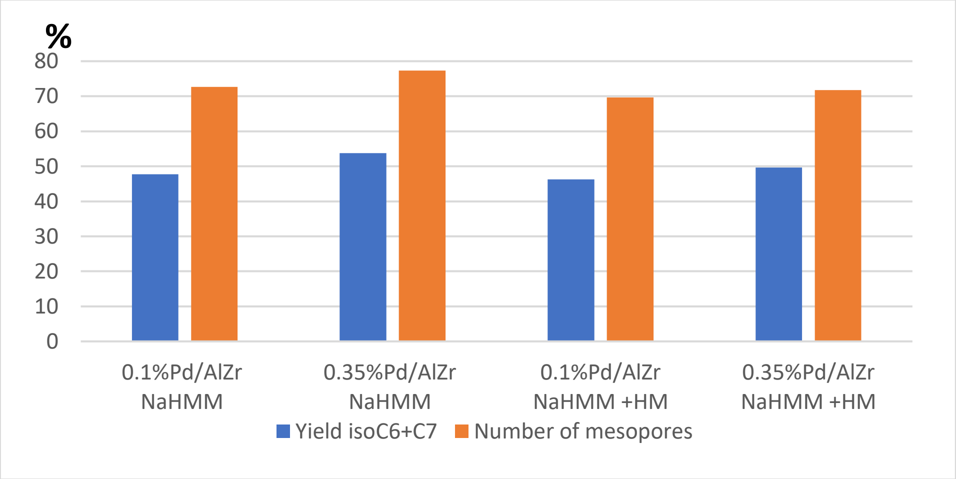


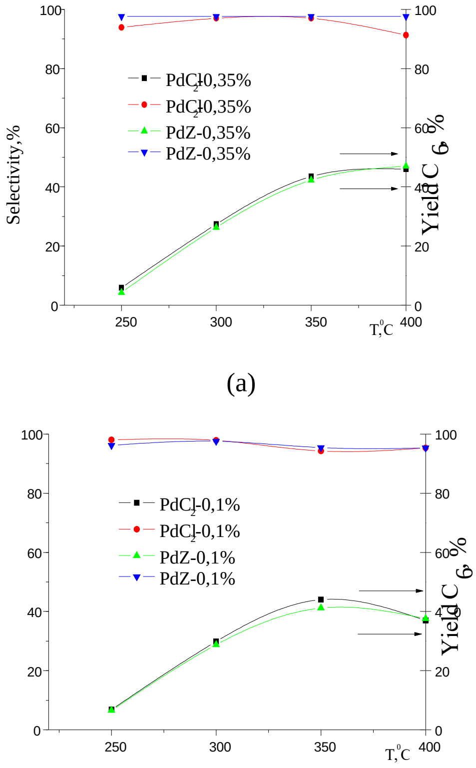
Figure 3. Effect of the number of mesopores on the C6+C7 isomers yield

Corresponding Author E-mail: djumabaevals@mail.ru

As can be seen from Fig. 3, the maximum yield of isomerization products is observed on the 0.35% Pd/AlZrNaHMM having the highest number of mesopores (77.3%).

As for the Pd-sol catalysts, the maximum conversion of n-hexane is observed on the 0.35% Pd-catalyst at 400^0C, which is 59.5%, while it decreases to 45.5% on the 0.1% Pd-catalyst at 400^0C.

Fig.4 shows comparative isohexanes yield, selectivity to isomers on 0.35% and 0.1% Pd obtained by impregnation with a solution of $PdCl_2$ and Pd-sol depending on temperature.



(a)

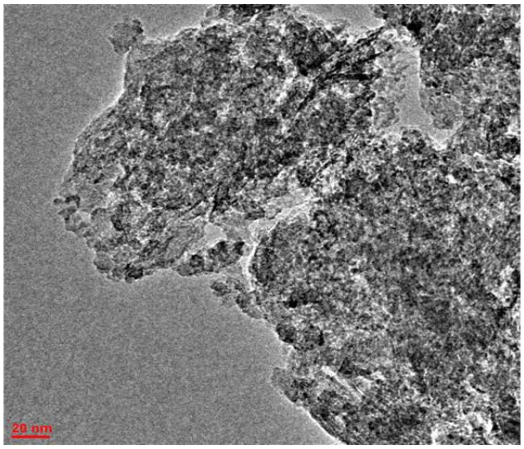
(b)

Figure 4. Isohexanes yield and selectivity of n-haxane isomerization on 0.35%PdZ/AlZrNaHMM and 0.35%Pd/AlZrNaHMM (a); 0.1%PdZ/AlZrNaHMM and 0.1%Pd/AlZrNaHMM (b) catalysts, depending on the process temperature.

Fig. 4 shows that the isohexanes yield and selectivity to isomers on the $PdCl_2$ and Pd-sol catalysts are almost the same. The C_6-isomers yield on the PdZ- and Pd-catalysts is 47% and 46%, respectively. A slightly increased isomerization activity of Pd-sol catalysts can be explained by a large number of average acid sites on this catalyst as compared with the Pd-catalyst from $PdCl_2$ (Table 2).

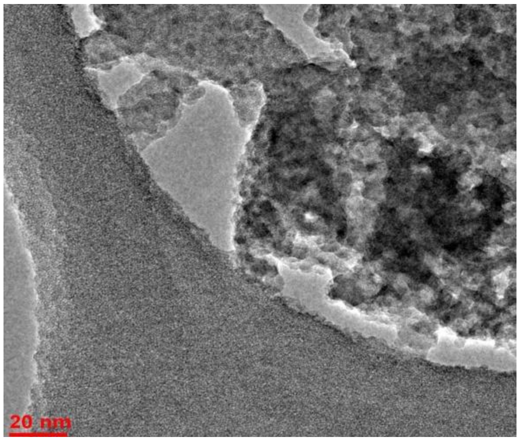
The synthesized catalysts were studied using an electron transmission microscope (Fig. 5) to understand the effect of the palladium particles dispersion on their isomerizing activity. As can be seen from the given images, the size of metal particles and their distribution on the surface of the support differs little for the two types of catalysts. Small palladium particles are uniformly distributed over the surface of the pillared montmorillonite. However, the palladium sol-based catalyst is characterized by a large number of accumulation of metal particles as compared with the $PdCl_2$-based catalyst.

The electron micrograph of the 0.35% Pd/AlZrNaHMM+HM-catalyst with a significant magnification (Fig. 6) shows that the particle size of palladium in this catalyst, found for two different areas of the catalyst, varies from 2.7 to 5.2 nm. The narrow size distribution of Pd particles demonstrates the decisive effect of the uniform pore size distribution in pillared montmorillonite on the size of metal particles.



(a)

Corresponding Author E-mail: djumabaevals@mail.ru



(b)

Figure 5. TEM images of 0.35%Pd /AlZrNaHMM +HM(a); 0.35%Pd-sol/AlZrNaHMM+HM (b).

As can be seen from Fig. 6, the particle size does not exceed 2.7-5.2 nm. Previously it was showed that reduction of Pd (2+) polyhydroxocomplexes in the presence of Mo (6+) polyoxoanions forms stable Pd-sols with a size of 4.5-5.5 nm, which don't change when Pd-sols are deposited on supports [9]. We observed the similar pattern when Pd-sols were deposited on the pillared clay (Fig. 6).

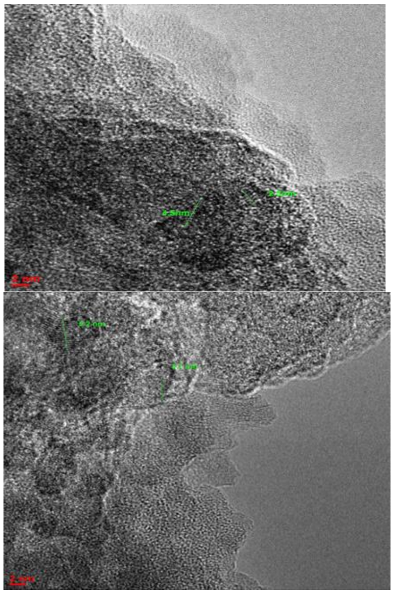


Figure 6. TEM images of 0.35%Pd /AlZrNaHMM +HM

4. CONCLUSION

The Pd-catalysts supported on pillared aluminum-zirconium Tagan (Kazakstan) montmorillonite (MM) from $PdCl_2$ and Pd-sol were synthesized and their textural, acidic and catalytic properties in the isomerization of n-hexane were investigated, depending on quantity of the active metal and the temperature. It was shown that the activity and selectivity of Pd catalysts in the isomerization of n-hexane change little with decreasing of palladium at different temperatures. The porous structure of the catalysts and the number of acidic sites of an average strength influence on the direction of the process itself and the yield of isomerization products. On the 0.35% Pd-catalyst at 400°C, the of C6 isomers is 46.0%, with a decrease of the palladium content to 0.1%, the isohexanes yield is 44.0% at a temperature of 350°C. The C6-isomers yield on the Pd-catalyst from sol is 47%, while on Pd it is 46%. A slightly increased isomerization activity of Pd-sol catalysts can be explained by a large number of average acid sites found on this catalyst as compared with the results obtained on the Pd-catalyst from PdCl2. The particle size of palladium in the 0.35% Pd/AlZrNaHMM + HM-catalyst found for two different areas of the catalyst varies quantity from 2.7 to 5.2 nm. The narrow size distribution of Pd particles demonstrates the decisive effect of the uniform pore size distribution in pillared montmorillonite on the size of metal particles. The pillared aluminum-zirconium Tagan montmorillonite containing Pd as an active phase demonstrates high activity and selectivity in the isomerization of n-hexane and this catalyst can be used in the n-alkanes hydroisomerization reaction.

5. ACKNOWLEDGMENT

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Corresponding Author E-mail: djumabaevals@mail.ru