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ВЕСТНИК

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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ISOMERIZATION OF H-HEXANE ON Pd CATALYSTS INFLICTED TO ACID-ACTIVATED MONTMORILLONITE IN Ca-FORM

Abstract. Pd/CaHMM catalysts have got and tested in the isomerization reaction of n-hexane. According to the results, in the palladium content decreased from 0.35% to 0.1% leads to a decrease in activity, but the selectivity of C_{4+} remains stable and high enough 99.6-100%. The maximum conversion of n-hexane by 0.35% Pd-catalyst is 45.1% at a temperature of 400°C, and 0.1% Pd-catalyst is 32.4% at the same temperature. One of the most important isomerization products is dimethyl butane; the maximum yield of 0.35% Pd contact is 21.3% at 350^0C. At a 0.1% Pd catalyst, the yield of dimethyl butane decreases and is 16.5% at 400°C. The introduction of mordenite significantly increases the activity and selectivity even on a low-percentage catalyst. At 0.35% Pd/CaHMM + HM catalyst, the conversion of n-hexane increases to 54.1% at 400°C, and the yield of 2.2-dimethylbutane is 25.8%. On a 0.1% Pd + HM catalyst, the conversion of n-hexane is 54.3%, and the maximum yield of dimethylbutane is 26.0% at 400^0C, which is slightly higher compared to 25.8% for 0.35% Pd.

The maximum yield of iso-hexanes on the non-zeolitic 0.35 and 0.1% Pd catalysts is 37.8 and 27.8%, respectively. Mordenite containing 0.35% Pd/CaHMM +HM catalyst reached 46.4%, at a low-percentage 0.1% Pd + HM catalyst 45.8%.

The increase in the octane number increases with increasing process temperature, as well as on catalysts modified with mordenite. The maximum increase was observed at 0.35% Pd/CaHMM + HM.

Keywords: isomerization, n-hexane, activated montmorillonite, catalyst, palladium.

Introduction. Natural layered silicates (clays) have the ability to ion exchange, high cation exchange capacity, micro-, meso and nanoporous structure, have surface active centers of various types that are widely used as high-performance components for the preparation of catalysts [1-3]. Montmorillonite (MM) is one of the most interesting representatives of layered silicates, the structural features and properties of which determine the wide possibilities of its use as a catalyst carrier are different processes. A characteristic property of montmorillonite clays is a high cation exchange capacity – from 60 to 150 meq / 100 g [4, 5].

It is known that acid treatment of clay minerals leads to a sharp increase in their catalytic and adsorption capacity [6-9]. The results of the study of samples by the method of low-temperature adsorption of nitrogen showed an increase in the specific surface area and a slight increase in the pore diameter. According to the data of the X-ray diffraction study, the crystal structure of the samples activated by solutions of mineral acids of low and medium concentration is preserved, and the results of the chemical analysis of natural clays after acid activation showed complete washing out of sodium ions from the structure of the samples and dissolution of a significant part of the octahedral magnesium, iron and aluminum cations, as a result of which the SiO2 content in the samples increases [10, 11]. In the case of MM, acid treatment often also causes a rather strong decrease in the first basal reflexes [12].

The determining factor in increasing the adsorption capacity of natural clay minerals after their acid treatment is the non-changing porous characteristics of MM, and the growth of the specific surface and the dissolution and removal of all possible impurity phases leading to the production of a monomineralic product, the destruction of the secondary structure, the increase in the accessibility of the adsorbed component to the surface of the adsorbent and appearance of silica gel. Natural clays are one of the available types of catalyst carriers for the reaction of isomerization of n-alkanes [13, 14]. In turn, as is known, structural isomerization of n-alkanes is one of the most demanded catalytic processes for obtaining high-octane additives to motor fuels [15-18]. The aim of this work was to study the texture, acid properties of Pd catalysts supported on activated montmorillonite in Ca-form, depending on the content of the active metal from $PdCl_2$ and the introduction of mordenite.

Experimental part

In the work, carefully used montmorillonite clay of the Tagan deposit without isolation of mono-mineral fraction of montmorillonite. The H-form of Tagansky montmorillonite was obtained by treatment with a solution of H_2SO_4, followed by washing from SO_4^{2-} ions. The activated clay was formed, dried in a thin layer first at room temperature, then at 150°C and then subjected to calcination at 500°C [19, 20]. The prepared H-form of MM was used as a support for Pd catalysts.

The catalysts were prepared by impregnating the support with aqueous solutions of $PdCl_2$ followed by drying, calcining and reduction of the oxides to the metallic state. The metal content in the samples was 0.1 and 0.35%. The textural characteristics of the samples were determined by the BET method for low-temperature nitrogen adsorption on the ACCUSORB instrument. Elemental analysis of the composites was carried out with the help of energy dispersive X-ray fluorescence spectroscopy on the energy dispersive microanalysis system INCA-Energy 450 mounted on a scanning electron microscope JSM6610LV, JOEL, Japan. The activity of the samples in the isomerization of n-hexane was investigated in a flow reactor with varying the process temperature in the range 250-400 ^{0}C. The process was carried out in a hydrogen flow at a feed rate of 0.82 hour^{-1}.

Results and its discussion

In table 1, there is data on the elemental composition of the initial calcium and activated H-form Tagan montmorillonite, catalysts with different Pd content (0.1%, 0.35%) and modified with mordenite.

Table 1 – Element composition of initial and activated montmorillonite and Pd / CaHMM
with different content of Pd and modified with mordenite (NM)

№	Example	C	O	Na	Mg	Al	Si	S	Ca	Ti	Fe	Pd	Итог
1	CaMM	14,35	46,40	0,25	2,20	10,53	23,46		1,30	0,13	1,37		100
2	CaHMM	14,27	45,50		2,08	10,78	24,55		0,69	0,18	1,94		100
3	0,1%Pd/ CaHMM	4,29	50,97		1,41	14,35	26,94	0,05	0,29	0,19	1,23	0,27	100
4	0,35%Pd/CaHMM	5,13	49,48		1,47	14,20	27,39	0,06	0,28	0,20	1,23	0,57	100
5	0,1%Pd/ CaHMM+HM	4,70	49,23		1,06	13,56	29,77	0,06	0,24	0,15	0,98	0,24	100
6	0,35%Pd/CaHMM+HM	5,87	51,21	0,07	1,06	12,20	27,90	0,04	0,18	0,13	0,76	0,57	100

From the analysis of the data in table 1, it follows that the acid activation of CaMM leads to the removal of sodium from the clay, only small amounts of sodium are found in the sample (6). After acid activation and Pd supported, the amount of calcium and magnesium is significantly reduced. According to the elemental analysis, several overestimated amounts of palladium are found in comparison with the impregnation method introduced.

In table 2, there is a data on the hydroisomerization of n-hexane by 0.35% and 0.1% Pd / CaHMM catalysts at different temperatures.

Tests of 0.35% and 0.1% of palladium catalysts showed that the activity decreases with decreasing palladium content, and the isomer selectivity practically does not change. As can be seen from table 2, the conversion of n-hexane increases with increasing temperature and reaches 45.1% on 0.35% Pd-catalyst, and on 0.1% Pd-catalyst is 32.4% at 400^{0}C. The selectivity for C_{4+} isomers at 400^{0}C is very high 99.6-99.7%. The maximum yield of dimethylbutane is observed at 350^{0}C on 0.35% Pd-contact and is 21.3%.

Table 2 – Isomerization of n-hexane on Pd / CaHMM-composite catalyst

Kat.	T, ^{0}C	α, %	S_{C6}, %	S_{C4+}, %	Yield reaction, %					
					{C_1-C_4	i-Б	2M Б	2,2Д МБ	2МП	Amount C_7
0,35% Pd	250	8,6	69,6	100	–	0,15	0,25	3,60	2,42	2,24
	300	22,4	83,6	100	–	–	0,56	11,2	7,4	3,11
	350	43,3	90,1	99.7	0,15	0,16	0,97	21,3	16,5	3,0
	400	45,1	81,7	99.6	0,18	0,32	0,69	17,8	15,5	7,0
0,1% Pd	250	6,5	74,3	100	–	–	0,2	2,9	1,9	1,5
	300	18,7	84,8	100	–	0,1	0,2	9,4	6,4	2,6
	350	23,5	87,3	99,6	0,1	0,2	0,5	12,6	8,0	2,2
	400	32,4	86,0	99.7	0,1	0,2	0,9	16,5	11,3	3,4
C_7 - 2,2 DMP - 2,2-Dimethylpentane; 2,4 DMP - 2,4-Dimethylpentane; 2,2,3TMB - 2,2,3-Trimethylbutane; 3,3DMP - 3,3-Dimethylpentane; 2MG-2-Methylhexane; 3MG-3-Methylhexane; 3 EP-3-Ethylpentane.										

When the palladium content is reduced to 0.1%, the yield of C_6-disubstituted isomers is reduced and is 16.5% at 400 °C. The yield of hydrocracked products does not exceed 0.18%. On a 0.35% Pd catalyst at 350^{0}C, the C_6 isomer content is 37.8%, with a decrease in palladium content of up to 0.1%, the isohexane yield is 27.8% at 400^{0}C.

Data on the yield of isohexanes, selectivity and conversion of the process of isomerization of n-hexane by 0.35% and 0.1% Pd-contacts at different temperatures are illustrated in figure 1.

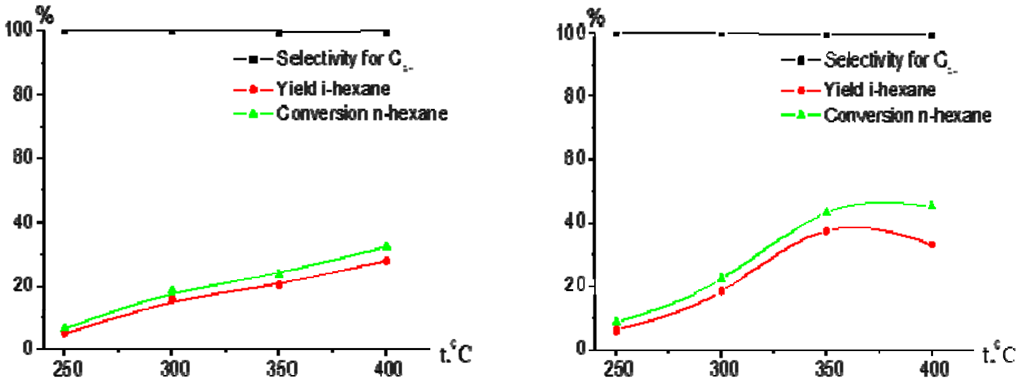

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Figure 1 – Isohexane yield, selectivity and conversion of the isomerization of n-hexane
by 0.1% Pd / CaHMM (1); 0.35% Pd / CaHMM (2) catalysts depending on the process temperature

The tests of 0.35% and 0.1% palladium catalysts showed that their activity decreased insignificantly with decreasing palladium concentration. The conversion of n-hexane and the yield of isomers increase with increasing temperature on both catalysts and at 350^{0}C reach constant values on 0.35% and 0.1% Pd at 400^{0}C.

The presence of C_7-isomers in reaction products probably indicates side processes in the isomerization of n-hexane.

Table 3 and figure 2 show some of the physicochemical characteristics of palladium catalysts based on activated montmorillonite.

As you can see from table 2, when the clay is activated, the specific surface of the sample rises from 89.2 to 99.2 m^2/g. With the addition of palladium, the specific surface area and the total pore volume increase, a Pd content reduction of up to 0.1% on Pd/CaHMM leads to an increase in the specific surface area of the sample from 107.8 to 127.6 m^2/g. The total pore volume rises from 0.095 to 0.117 cm^3/g.

The changing porous structure is clearly illustrated by figure 2.

Table 3 – Specific surface area and effective pore volume and their distribution for Pd / CaHMM-catalyst

Example	S, m^2/g	Total pore volume, $см^3/г$	R, Å	Relative quantity , %	
				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
0,35%Pd/CaHMM	107,8	0,095	10,0-70,0	47,3	52,7
0,1%Pd/CaHMM	127,6	0,117	10,0-68,0	57,1	42,8

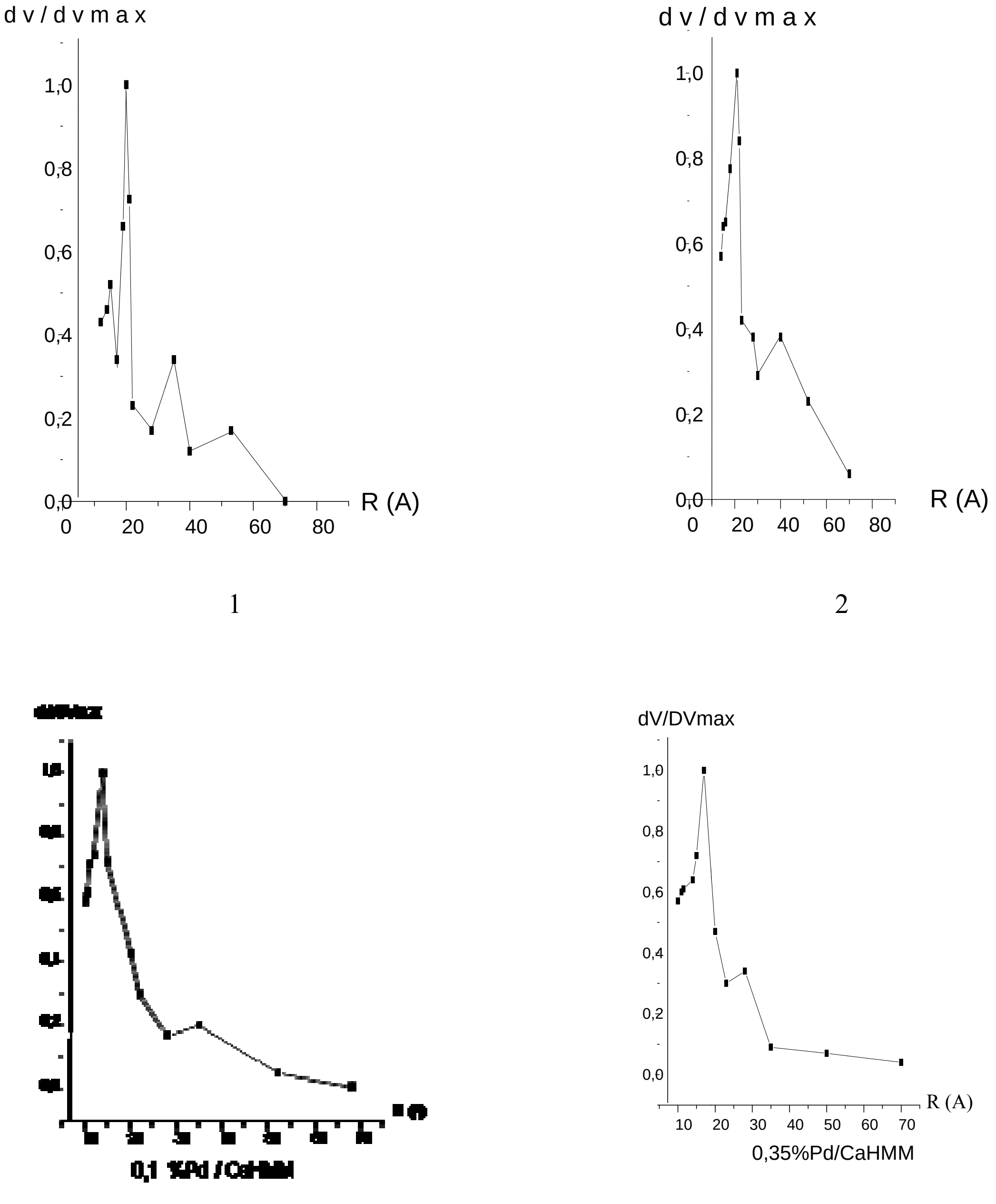

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Figure 2 – Pore distribution curves for their effective radius in the Pd / CaHMM-composite catalyst depending on the metal content of CaHMM (1).
The signs of the curves: CaMM (1); CaHMM (2); 0.1% Pd / CaHMM (3); 0.35% Pd / CaHMM (4)

Calculation of pore size distribution showed that when Pd content is reduced to 0.1%, the amount of mesopores decreases from 52.7 to 42.8%, and the number of micropores increases from 47.3 to 57.1%, which is reflected in a decrease in activity.

Table 4 and figure 3 show the isomerization activity of Pd / CaHMM + HM, modified with mordenite depending on the metal content.

Table 4 – Isomerization of n-hexane on Pd / CaHMM + HM-composite catalyst

Kat.	T, ^{0}C	α, %	S_{C6}, %	S_{C4+}, %	Yield reaction, %					
					{C_1-C_4	i-Б	2М Б	2,2Д МБ	2МП	Amount C_7
0,35% Pd+HM	250	7,9	81,6	100	–	–	0,2	3,9	2,5	1,3
	300	27,0	94,2	100	–	0,2	0,4	15,6	9,8	0,9
	350	41,0	93,3	99,7	0,1	0,3	1,0	22,8	15,4	1,3
	400	54,1	85,7	99,8	0,1	0,2	2,4	25,8	20,6	5,0
0,1% Pd+HM	250	9,2	86,0	100	–	–	0,2	4,8	3,2	1,08
	300	33,3	92,3	99,9	0,04	0,15	0,6	18,0	12,2	1,8
	350	51,1	93,8	99,8	0,1	0,3	0,5	26,3	19,7	2,27
	400	54,3	88,9	99,7	0,16	0,4	0,4	26,0	19,8	5,12

Iso-C_7: 2.2 DMP – 2,2-Dimethylpentane; 2,4 DMP – 2,4-Dimethylpentane; 2,2,3TMB – 2,2,3-Trimethylbutane; 3,3DMP – 3,3-Dimethylpentane; 2MG-2-Methylhexane; 3MG-3-Methylhexane; 3 EP-3-Ethylpentane.

The incorporation of mordenite into Pd / CaHMM significantly increases its isomerizing activity and isomer selectivity. Over 0.35% Pd / CaHMM + HM catalyst, the maximum yield of isohexanes is observed at 400^{0}C, which reaches 46.4%, with the yield of 2,2-dimethylbutane being 25.8%. The conversion of n-hexane increases to 54.1% with a C_{4+}- selectivity equal to 99.8%. For comparison, the maximum yield of isohexanes on zeolite-free 0.35 and 0.1% Pd-catalysts is much lower and is 37.8 and 27.8%, respectively (table 2). On 0.1% Pd + HM catalyst, the maximum yield of dimethylbutane from n-hexane is 26.0% at 400^{0}C versus 25.8% for 0.35% Pd. According to the total content of C_6-isomers (45.8%), 0.1% Pd-catalyst is only slightly inferior to 0.35% Pd (46.4%). It was found that in the investigated temperature range the selectivity for the C_{4+} isomers for all catalysts remains quite high 99.7-100%. At the same time, the yield of hydrocracking products does not exceed 0.1% on 0.35% Pd/CaHMM + HM at 400^{0}C.

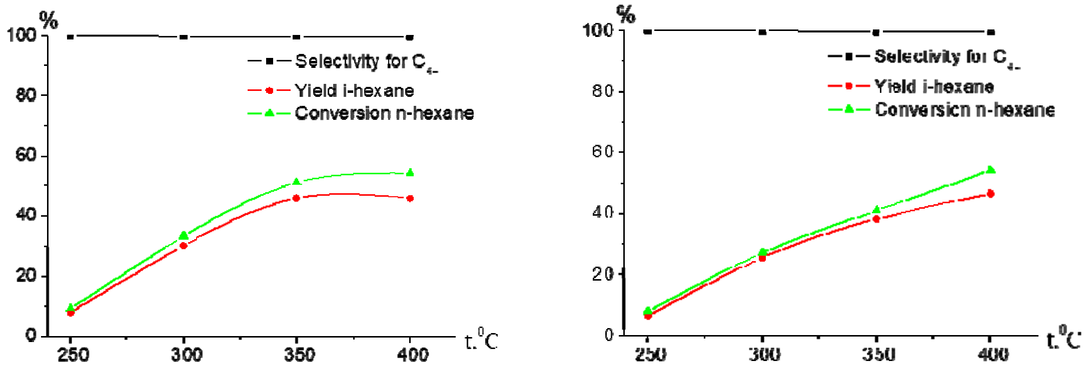

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Figure 3 – Isohexane yield, selectivity and conversion of the isomerization process of n-hexane on 0.1% Pd / CaHMM + HM (1); 0.35% Pd / CaHMM + HM (2) catalysts depending on the process temperature.

Based on the data of low-temperature nitrogen adsorption (BET), the texture characteristics of Pd-catalysts modified with mordenite were determined.

As you can see from Table 5, the addition of mordenite to palladium catalysts supported on CaHMM + HM leads to a significant increase in the specific surface area for 0.35% Pd from 107.8 (table 3) to 129.4 m^2/g (table 5), the effective pore volume is increased from 0.095 to 0.101 ml/g. In the case of 0.1% Pd, modifying

Table 5 – Comparative structural and adsorption characteristics of Pd-contacts based on CaHMM modified with mordenite

Example	S, m^2/g	Total pore volume, sm^3/g	R, Å	Relative quantity , %	
				Micropores, (0-20Å)	Mesopores, (20-80Å)
0,35% Pd/CaHMM+HM	129,4	0,101	10,0-68,0	52,0	48,0
0,1% Pd/CaHMM+HM	159,2	0,125	10,0-74,0	51,9	48,1

with mordenite leads to an even more significant growth of the specific surface: from 127.6 to 159.2 m^2/g, and an effective pore volume from 0.111 to 0.125 cm^3/g. The growth of the specific surface and pore volume is accompanied by a small a change in pore size distribution, with the number of micropores slightly higher (52.0-51.9%) than mesopores (48.1-48.0%), regardless of the palladium content.

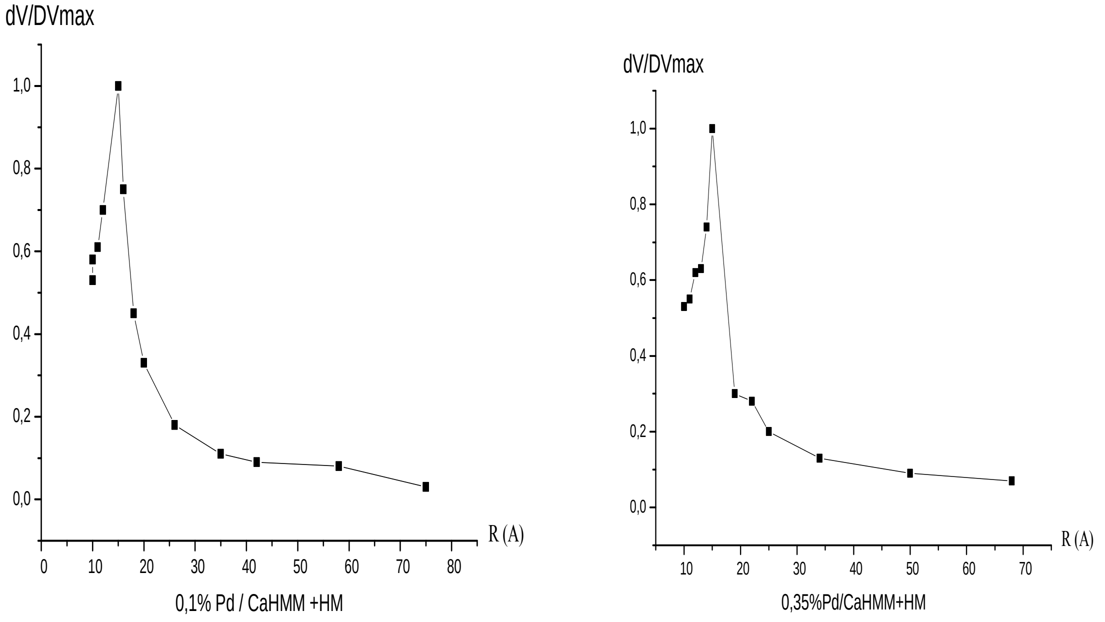

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Figure 4 – Pore distribution curves for their effective radii on a Pd / CaHMM +HM composite catalyst, depending on the metal content.
Signs of the curves: 0.1% Pd / CaHMM + HM (1); 0.35% Pd / CaHMM +HM (2)

Thus, the introduction of mordenite into the catalyst results in a change in the texture characteristics of the Pd catalysts. The substantial growth of the isomerizing activity and yield of C_6 and C_7 isomers in the isomerization of n-hexane is probably due to an increase in the specific surface area and the number of mesopores when modifying with mordenite. Thus, on 0.1% Pd/CaHMM + HM, the mesopore number increases from 42.8% to 48.0%. On this catalyst, the maximum conversion of n-hexane is observed, equal to 54.3% at 400° C. There is a correlation between the isomerizing activity and the amount of dimethyl-butanes formed on Pd-catalysts with the amount of mesopores.

Figure 5 shows the dependence of the increase in the octane number (o.n.) of isomerization products of n-hexane on palladium catalysts, depending on the Pd content and upon modification with mordenite.

As can be seen from Fig. 5, the increase in the octane number significantly increases with an increase of the process temperature and on the catalysts modified by mordenite, which is due to the growth of yields formed from n-hexane isomers, including disubstituted, with high octane numbers. The maximum increase o.n. was observed on 0.35% Pd/CaHMM + HM.

Based on the results, it is possible to conclude that the Pd catalysts supported on acid-activated montmorillonite in Ca-form are promising, which are characterized by high isomerizing activity and selectivity during the hydroconversion of n-hexane to produce high-octane isomers.

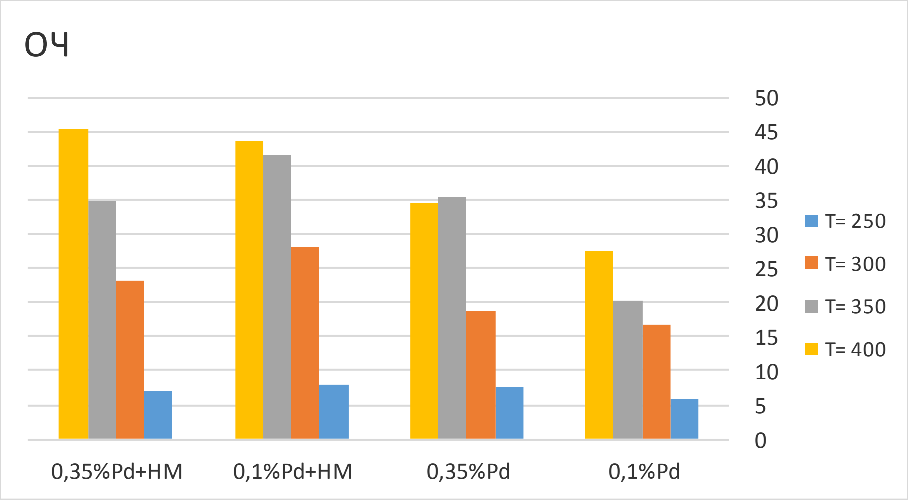

Figure 5 – Temperature dependence of the increase in the octane number of isomerization products of n-hexane on the 0.35% PdCaHMM and Pd/CaHMM +HM catalysts studied by the calculation method

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н-ГЕКСАНДЫ Ca-ФОРМАДАҒЫ ҚЫШҚЫЛДЫ-БЕЛСЕНДІРІЛГЕН МОНТМОРИЛЛОНИТКЕ ЖАҒЫЛҒАН Pd-КАТАЛИЗАТОРЛАРДА ИЗОМЕРЛЕУ

Аннотация. Pd/CaHMM катализаторлары алынып және н-гександы изомерлеу реакциясында сыналған болатын. Алынған нәтижелер бойынша анықталғаны: палладийдің мөлшерін 0,35%-дан 0,1%-ға азайту белсенділіктің төмендеуіне әкеледі, алайда C_{4+} бойынша тұрақты және барынша жоғары болып қалады - 99,6-100%. Н-гексанның 0,35% Pd-катализаторындағы ең жоғары конверсиясы 400^{0}С температура жағдайында 45,1%, ал 0,1% Pd–катализаторында тура сол температура жағдайында 32,4% құрайды. Измерлеудің аса маңызды өнімдерінің бірі диметилбутан болып табылады, 0,35% Pd-жанасудағы ең көп шығуы 350^{0}С жағдайында 21,3% құрайды. 0,1% Pd-катализаторында диметилбутанның шығуы азайып және 400^{0}С жағдайында 16,5% құрайды. Морденитті қосу тіпті төмен пайызды катализатордың өзінде белсенділік пен селективтілікті едәуір арттырады. 0,35%Pd/CaHMM+HM-катализаторында н-гексанның конверсиясы 400^{0}С жағдайында 54,1%-ға артады, ал 2,2-диметилбутанның шығуы 25,8% құрайды. 0,1%Pd+HM-катализаторда н-гексанның конверсиясы 54,3%-ды, ал диметилбутанның ең көп шығуы 400^0 жағдайында 26,0% құрайды, бұл 0,35% Pd катализаторындағы 25,8% мөлшерімен салыстырғанда аздап жоғары.

Изогександардың цеолитсіз 0,35 және 0,1% Pd-катализаторларда ең көп мөлшерде шығуы соған сәйкес 37,8 және 27,8% құрайды. Құрамында моргениті бар 0,35%Pd/CaHMM+HM-катализаторда C_6-изомерлердің шығу мөлшері 46,4%, төмен пайызды 0,1%Pd+HM катализаторда 45,8% құрайды.

Октандық санның өсуі процестің температурасы өскен сайын, сондай-ақ морденитпен түрлендірілген катализаторларда артып отырады. Октандық санның барынша өсуі 0,35% Pd/CaHMM +HM катализаторында байқалды.

Түйін сөздер: изомерлеу, н-гексан, белснедірілген монтмориллонит, катализатор, палладий.

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ИЗОМЕРИЗАЦИЯ Н-ГЕКСАНА НА Pd-КАТАЛИЗАТОРАХ, НАНЕСЕННЫХ НА КИСЛОТНО-АКТИВИРОВАННЫЙ МОНТМОРИЛЛОНИТ В Ca-ФОРМЕ

Аннотация. Были получены и испытаны Pd/CaHMM-катализаторы в реакции изомеризации н-гексана. По полученным результатам было отмечено, что снижение содержания палладия с 0,35% до 0,1% приводит к снижению активности, но селективность по C_{4+} остается стабильной и достаточно высокой 99,6-100%. Максимальная конверсия н-гексана на 0,35% Pd-катализаторе составляет 45,1% при температуре 400^{0}С, а на 0,1% Pd-катализаторе составляет 32,4% при этой же температуре. Одним из важнейших продуктов изомеризации является диметилбутан, максимальный выход на 0,35% Pd-контакте составляет 21,3% при 350^{0}С. На 0,1% Pd-катализаторе выход диметилбутана снижается и составляет 16,5% при 400^{0}С. Введение морденита заметно повышает активность и селективность даже на низкопроцентном катализаторе. На 0,35%Pd/CaHMM+HM-катализаторе, конверсия н- гексана растет до 54,1% при 400^{0}С, а выход 2,2-диметилбутана составляет 25,8%. На 0,1%Pd+HM-катализаторе конверсия н- гексана составляет 54,3%, а максимальный выход диметилбутана 26,0% при 400^0, что незначительно выше по сравнению с 25,8% на 0,35% Pd.

Максимальный выход изогексанов на бесцеолитных 0,35 и 0,1% Pd-катализаторах составляет 37,8 и 27,8% соответственно. На морденит, содержащем 0,35%Pd/CaHMM+HM-катализаторе выход C_6-изомеров достигает 46,4%, на низкопроцентном 0,1%Pd+HM катализаторе 45,8%.

Прирост октанового числа растет с увеличением температуры процесса, а также на катализаторах, модифицированных морденитом. Максимальный прирост о.ч. наблюдался на 0,35% Pd/CaHMM+HM.

Ключевые слова: изомеризация, н-гексан, активированный монтмориллонит, катализатор, палладий.

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