ХИМИКО-ТЕХНОЛОГИЧЕСКИЕ НАУКИ И ЭКОЛОГИЯ. НЕФТЕГАЗОВАЯ ИНЖЕНЕРИЯ

УДК 54-44/661.715.2/665.612.2
МРНТИ 31.15.28

SUPPORTED PLATINUM CATALYSTS IN THE DEHYDROGENATION OF MIXTURE OF LIGHT ALKANES IN THE REDUCING MEDIUM

S.R. KONUSPAYEV [1], A.R. BRODSKY [2], D.B. TLEUGABYLOVA[1], A.T. AITZHAN[1], E.D. ASHIMOVA[1], E.S. AKAN[1]

[1]Al-Farabi Kazakh National University
[2]D.V.Sokolskiy Institute of Fuel, Catalysis and Electrochemistry

Abstract: *Mixtures of light alkanes simulate associated gas of oil production, the problem of processing of which remains relevant both in the world and in Kazakhstan. New supported catalysts based on platinum metals have been proposed for the dehydrogenation reaction of a mixture of light alkanes to the corresponding olefins prepared by the impregnation method according to moisture capacity. The structure of freshly prepared and spent catalysts 3% Pt, Pd, Ru on $\gamma - Al_2O_3$ were prepared by physicochemical methods TEM, SEM, BET. The particle size distribution curves were made up to determine the distribution of particles on the surface of the catalysts. The conversion of a mixture of light alkanes in a reducing environment was carried out in a laboratory flow-type installation on a stationary catalyst bed at atmospheric pressure. The conversion of a mixture of light alkanes on platinum metals supported on $\gamma - Al_2O_3$ in four modes is presented on comparative tables in the temperature range of 350–600°C. The highest yield was observed at 3% Ru / $\gamma - Al_2O_3$ with the joint feeding of a light alkanes mixture with water at 500°C. Water does not participate in the composition of the final reaction products but shifts the equilibrium in the system, forming dissipative structures on the catalyst surface.*

Keywords: *dehydrogenation, catalyst, lower alkanes, hydrogen, ethylene, propylene, olefins*

ТОТЫҚСЫЗДАНДЫРУ ОРТАДА ЖЕҢІЛ АЛКАНДАР ҚОСПАЛАРЫН ДЕГИДРЛЕУ КЕЗІНДЕ ОТЫРҒЫЗЫЛҒАН ПЛАТИНА МЕТАЛДАРЫ

Аңдатпа: *Мұнаймен бірге өндірілетін ілеспе газдың құрамындағы жеңіл алкандардың қоспаларын өңдеу проблемасы әлемде де, Қазақстанда да өзекті проблема болып табылады. Жеңіл алкандардың қоспасын тиісті олефиндерге дегидрлеу үшін, ылғал сыйымдылығы бойынша сіңдіру әдісімен платиналы металдар негізіндегі тасымалдағышқа отырғызылған жаңа катализаторлар ұсынылды. Жаңа дайындалған және қолданылған катализаторлардың құрылымы γ–Al_2O_3 тасымалдағышына отырғызылған 3% Pt, Pd, Ru ПЭМ, РЭМ, БЭТ физика-химиялық әдістерімен зерттелді. Катализаторлардың бетінде бөлшектердің таралуын анықтау үшін белгілі бір өлшемдер бойынша қисықтар тұрғызылды. Жеңіл алкандардың қоспасын тотықсыздану ортасында түрлендіру атмосфералық қысымда, катализатордың стационарлық қабатында ағынды типті зертханалық қондырғыда жүргізілді. γ–Al_2O_3 тасымалдағышына отырғызылған платина негізіндегі металдардағы жеңіл алкандардың қоспасын конверсиялаудың салыстырмалы кестелері берілген, олар төрт режимде, 350–500°C температура аралығында істелінді. Алынған өнімнің ең үлкен шығымы 3% Ru/γ–Al_2O_3 катализаторында жеңіл алкандардың қоспасын 500°C-та сумен бірге беру кезінде байқалды. Су реакцияның соңғы өнімдерінің құрамына қатыспай, катализатордың бетінде диссипативті құрылым құра отырып, жүйедегі тепе-теңдікті ығыстырады.*

Түйінді сөздер: *дегидрлеу, катализатор, төменгі алкандар, сутек, этилен, пропилен, олефиндер*

НАНЕСЕННЫЕ ПЛАТИНОВЫЕ МЕТАЛЛЫ ПРИ ДЕГИДРИРОВАНИИ СМЕСИ ЛЕГКИХ АЛКАНОВ В ВОССТАНОВИТЕЛЬНОЙ СРЕДЕ

Аннотация: *Смеси легких алканов моделируют попутный газ нефтедобычи, проблема переработки которых остается актуальной как в мире, так и Казахстане. Предложены новые нанесенные катализаторы на основе платиновых металлов для реакции дегидрирования смеси легких алканов в соответствующие олефины, приготовленные методом пропитки по влагоёмкости. Структура свежеприготовленных и отработанных катализаторов 3% Pt, Pd, Ru на γ–Al_2O_3 были исследованы физико-химическими методами ПЭМ, РЭМ, БЭТ. Для определения распределения частиц на поверхности катализаторов были построены кривые распределения частиц по размерам. Превращение смеси легких алканов в восстановительной среде проводили на лабораторной установке проточного типа на стационарном слое катализатора при атмосферном давлении. Представлены сравнительные таблицы конверсии смеси легких алканов на платиновых металлах, нанесенных на γ–Al_2O_3 в четырех режимах, в интервале температур 350–500°С. Наибольший выход наблюдался на 3% Ru/γ–Al_2O_3 при совместной подачи смеси легких алканов с водой при 500°С. Вода, не участвуя в составе конечных продуктов реакции, смещает равновесия в системе, образуя на поверхности катализатора диссипативные структуры.*

Ключевые слова*: дегидрирование, катализатор, низшие алканы, водород, этилен, пропилен, олефины*

Introduction

The problem of associated gas processing is still relevant in the world. According to the World Bank, at the end of 2016, Kazakhstan is on the 14th place in terms of flaring associated gas. In 2016, about 2.7 billion cubic meters of gas were burned on torches in the Republic but this product could be used with a certain economic benefit. Associated gas is a valuable petrochemical raw material consisting of alkanes $C_1 – C_4$, it also contains significant amounts of hydrogen sulfide and other harmful impurities. The following factors prevent from successful processing of associated petroleum gas: the necessity of collection; separation from moisture, harmful impurities and delivery to the place of processing. All this requires significant processing costs due to the remoteness of oil fields from industrial centers.

The main method of associated gas processing is the conversion of alkanes to olefins, i.e. dehydrogenation. It is known that the need for olefins is growing and it is necessary to look for new ways to obtain them. Processing can be carried out in two directions: by oxidation of light alkanes with the production of olefins and hydrogen binding to water; in the reducing medium with the production of olefins and hydrogen. The second direction is preferable because both products are in demand in the economy. When selecting dehydrogenation catalysts in a reducing medium, hydrogenation catalysts were used [1], which at high temperatures carry out a diverse reaction and take into account the achievements of non-equilibrium thermodynamics [2]. Earlier in [3] we reviewed the platinum catalysts supported on aluminum oxide.

The authors provide information on the dehydrogenation of alkanes C_3-C_4 [4-6] to obtain the corresponding olefins. Thus, according to [4] it was found that the catalyst PtSnNa/γ–Al_2O_3 at a molar ratio Sn/Pt 6:1 shows the best rates of conversion of propane 26.97% and the selectivity of propylene is 99.18%.The authors of [5] prepared a catalyst PtSnK/γ–Al_2O_3 for the reaction of dehydrogenation of isobutane to isobutene and noted that the good indicators of the conversion of isobutane 46.59 ±0.83% and the selectivity of 99.34 ±0.49% are obtained when the ratio of Pt to Sn is 1:1 , the concentration of H_2PtCl_6 is 7.72 *10^{-4} mol/L, at the temperature of 500°C and content of K is 0.8%.

The researchers [6] studied the SnPt/ TiO_2 catalyst in the reaction of dehydrogenation of light alkanes. It was found that the structure and catalytic properties are closely related to the interaction between the metal and the carrier, which is regulated by heat treatment at different

temperatures and environments. According to the results of studies, the most active catalyst and the strongest interaction is formed in the reducing environment.

EXPERIMENTAL PART

The objects of study is a mixture of light alkanes, which is filled with gas cylinders in industry, consisting of a mixture of C_1 - C_4, in the text marked as MLA. MLA was not cleared of the number of deodorants that are added in order to make gas the smell since sulfur compounds are present in associated gases.

Experiments on the conversion (catalytic dehydrogenation) of light alkanes in the reducing medium were carried out on a laboratory installation of a flow-type with a fixed catalyst bed at atmospheric pressure.

The catalysts were prepared by the impregnation method according to the water capacity of the Pt, Pd, Ru salts to the granulated industrial $\gamma - Al_2O_3$.

The following procedure represents the preparation of the catalysts. Before applying the active metal, $\gamma - Al_2O_3$ granules were subjected to the following treatment, calcined at 400 °C for 4 hours to desorb substances that could be adsorbed during its storage. Then the capacity of the carrier was determined. The active metal was dissolved in a volume of water corresponding to the amount of water that the carrier can absorb. After impregnation, the catalyst was dried and experimentally reduced in a stream of hydrogen directly in the reactor.

RESULTS AND DISCUSSION

The conversion of a mixture of light alkanes was performed in the following modes. Mode № 1 — a mixture of light alkanes (MLA) was supplied to the catalyst reduced in the reactor. Mode № 2 — hydrogen was supplied with the MLA. Mode № 3 — water was supplied with the MLA and mode № 4 — hydrogen and water were supplied with the MLA.

The yield of olefins is shown in Table 1. The conversion of a mixture of light alkanes when passing through a bed of a reduced stationary catalyst is low and ranges from 1–2%, with increasing temperature from 350 to 500°C. When mixed together, the mixture of light alkanes and gaseous hydrogen rises, especially on ruthenium. The yield of olefins increases at 500 °C, for example, on platinum 6.2%, on palladium 4.0%, and on ruthenium 10.0% when the mixture of light alkanes is supplied with water. When a mixture consists of light alkanes, water, and hydrogen, the yield of olefins also increases on ruthenium at all temperatures between 6.6% and 7.4%. Water and hydrogen that are not involved in the formation of target products were introduced based on the achievements of non-equilibrium thermodynamics and we associate this with the formation of uniformly adsorbed dissipative structures on the surface, which, according to [2], create non-equilibrium conditions on the catalyst surface, which shifts the equilibrium towards the formation of the target products in our case olefins and hydrogen.

Table 1. Conversion of a mixture of light alkanes (MLA) on 3% of platinum metals supported on γ-Al_2O_3 granules in flow-type mode at atmospheric pressure, with the catalyst volume of 5 cm^3.

Mode		t°C		Feed rate, $hour^{-1}$		Olefin content , %.	
		MLA	H_2	H_2O	Ru	Pd	Pt
Without additives	350	120	-	-	0,2	1,4	0,4
	400	120	-	-	1,0	1,6	0,4
	450	120	-	-	1,2	2,0	1,0
	500	120	-	-	1,6	2,2	1,2
Hydrogen	350	120	50	-	1,6	1,6	0,8
	400	120	50	-	1,8	1,8	1,2
	450	120	50	-	2,0	2,0	1,8
	500	120	50	-	2,4	2,4	2,2
Water	350	120	-	620	2,0	2,0	1,2
	400	120	-	620	2,4	2,2	1,4
	450	120	-	620	2,6	3,4	2,4
	500	120	-	620	10,0	4,0	6,2
Water + hydrogen	350	120	50	620	6,6	2,0	1,4
	400	120	50	620	6,8	2,2	1,6
	450	120	50	620	6,9	3,0	2,6
	500	120	50	620	7,4	5,0	4,2

We studied the fresh and spent samples of catalysts to evaluate the active center of the catalyst. Scanning electron microscopy (SEM) makes it possible to estimate particle sizes on the surface of catalysts with varying degrees of resolution. SEM images were taken at an accelerating voltage of 20 kV, a resolution of 0.5 μm. SEM images for fresh and spent 3% Pd/Al_2O_3 catalysts are presented in Fig. 1 and 2. We observe a scaly-layered structure on the surface of the fresh catalyst (Fig. 1). This structure is preserved on the spent catalyst (Fig. 2), but it can be seen that the particles become noticeably larger, while there is some blurring between the particles, which is apparently due to the carbonization of the spent catalyst.

Similar images were taken for 3% Pt/Al_2O_3 and 3% Ru/Al_2O_3 (Fig. 3 and 4). Pictures of spent platinum and ruthenium catalysts in contrast to palladium are clearer, which, apparently, can be attributed to lower surface carbonization.

If the structure of the fresh and spent catalysts on the Pt/Al_2O_3 surface is the same (Fig.3), there is a change in the layered structure on the spent Ru/Al_2O_3 samples (Fig.4) to the needle one. At experimental temperatures in the range of 350–500 °C, ruthenium is recrystallized with a change in both the size and the crystalline form. Figure 4 (a) shows a scaly-layered surface, and on 4 (b) a needle-like structure.

The same samples of catalysts (3% Pd/Al_2O_3, 3% Pt/Al_2O_3, 3% Ru/Al_2O_3) were taken by

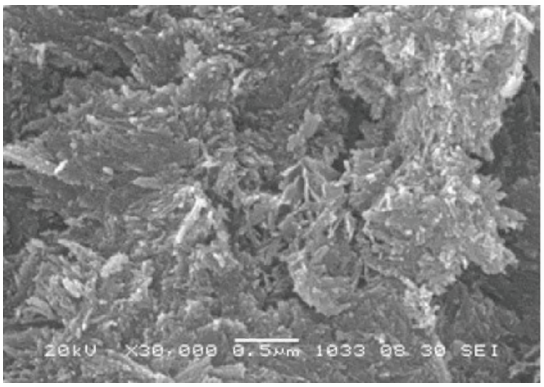

Fig. 1. SEM images of fresh 3% Pd/Al_2O_3

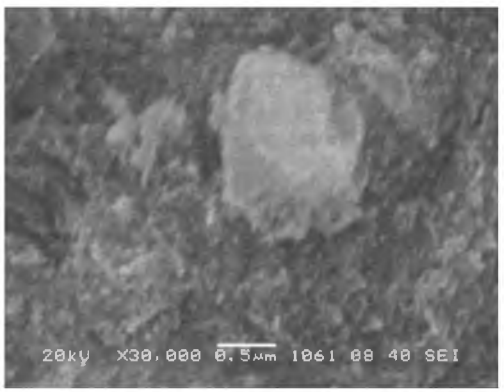

Fig. 2. SEM images of spent 3% Pd / Al_2O_3.

(a) (b)

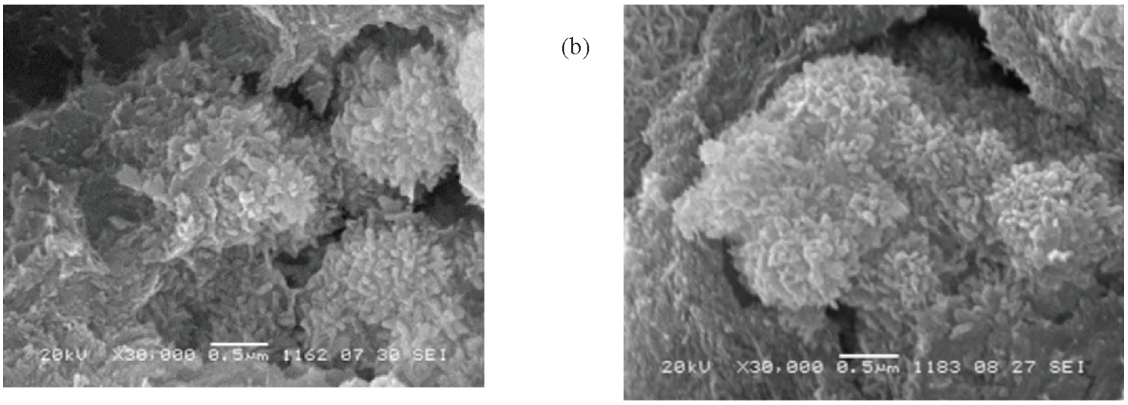

Fig. 3. SEM images of 3% Pt/Al_2O_3 (a) fresh and (b) spent catalyst.

(a) (b)

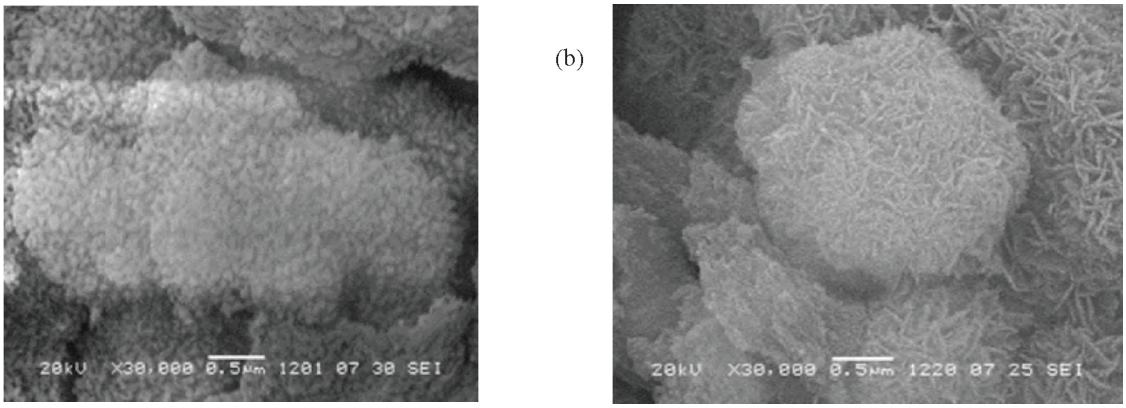

Fig. 4. SEM images of 3% Ru/Al_2O_3 (a) fresh and (b) spent catalyst.

(a) (b)

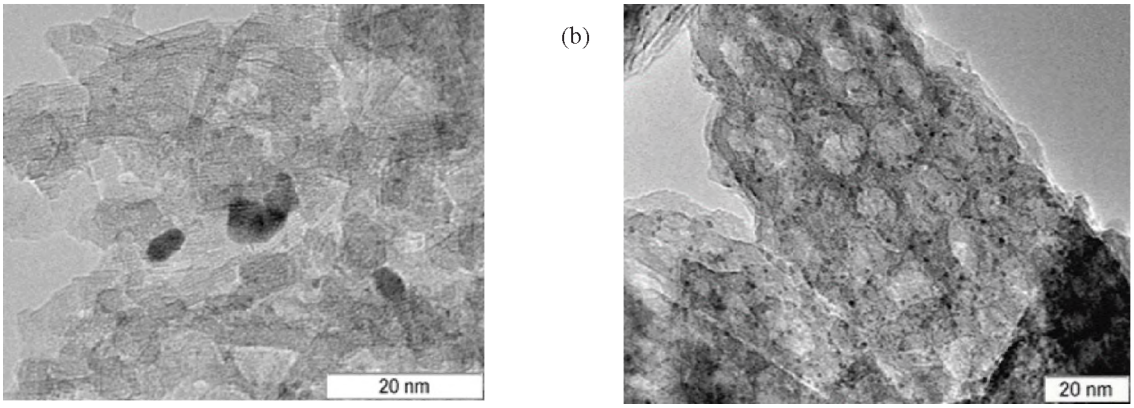

Fig. 5. TEM images of 3% Pt/Al_2O_3 (a) fresh and (b) spent catalyst.

(a) (b)

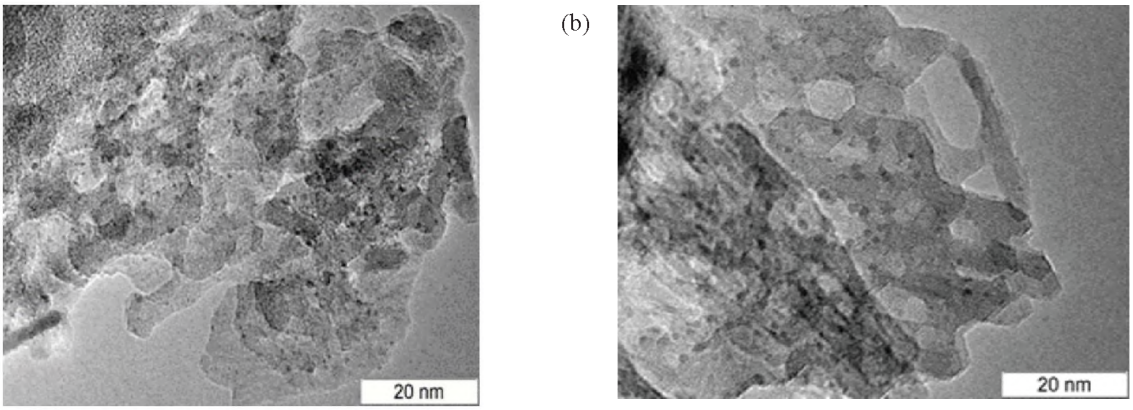

Fig. 6. TEM images of 3% Ru/Al_2O_3 (a) fresh and (b) spent catalyst.

transmission electron microscopy (TEM). Figure 5 and 6 show TEM images of platinum and ruthenium catalysts, where there are no significant differences between the fresh and the spent catalyst. We can observe a plain allocation of particles on the surface.

The SEM images were spent to plot the particle size distribution, a typical relationship is shown in Figure 7. The particle size varies from 1 to 9 mm and the maximum is 2.5 mm, similar dependencies are obtained on other catalysts, they differ in particle sizes and different maximum in size. The graph shows the dimensions in mm, which can be converted to real dimensions depending on the resolution of the images.

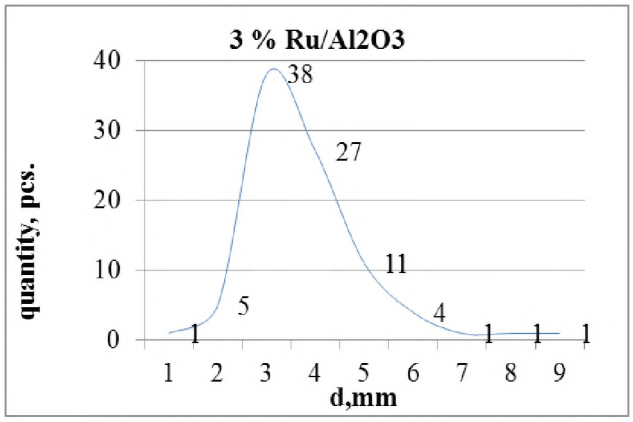

Fig. 7. Particle size distribution on the surface.

The prefix SEM makes it possible to determine the chemical composition of points. The reduced catalyst granule was split in half, as shown in Figure 8. The chemical composition was determined by the granule diameter at the marked points, which is presented in Table 2. On a fresh catalyst, the maximum ruthenium content on the granule surface is 2.22%. It was expected that the content of ruthenium would decrease towards the center of the granule. However, it turned out that ruthenium is almost evenly distributed in the volume of the granule. Moreover, in the fresh catalyst, the content of ruthenium varies between 1.72 and 1.82, and in the spent catalyst it shows 2.21 - 2.49%. At high temperatures, ruthenium is migrated over the γ-Al2O3 granule volume.

Table 2. The chemical composition of the points marked in Figure 8, according to the responses of the SEM spectra prefix

Number of points	Fresh 3 % Ru/Al_2O_3, Ru content	Spent 3 % Ru/Al_2O_3 Ru content
1	2.22	2.76
2	1.82	2.21
3	1.74	2.34
4	1.86	2.38
5	1.72	2.36
6	1.76	2.49
7	1.77	2.27

The values of specific surfaces of fresh and spent catalysts are presented in Table 3. The initial γ-Al_2O_3 was 209.5 m^2/g, a decrease in the specific surface area was observed in all cases. As for ruthenium, it is 179.1 m^2/g; palladium decreases to 133.9 m^2/g, and for platinum up to 168.9 m^2/g. Applying the metal on the carrier leads to a complex interaction in the surface, which decreases the total surface of the catalysts. An interesting picture is observed by comparing fresh and spent catalyst. In ruthenium and platinum, the surfaces of spent catalysts are reduced, which is associated with sintering and

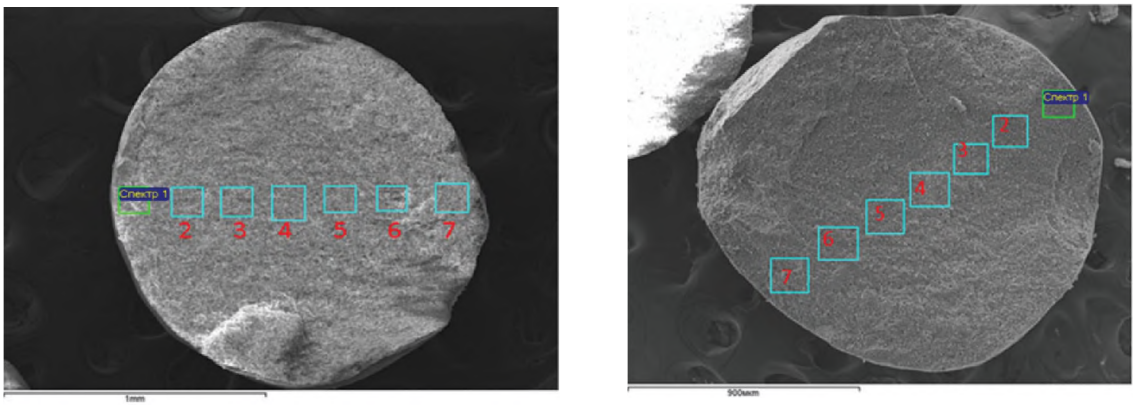

Fig.8. Chipped granules of fresh (a) and spent(b) catalyst 3% Ru / Al_2O_3

Table 3. Catalyst specific surfaces and pore sizes

Catalysts		SSA, m^2/g	Pore size, nm
γ-Al_2O_3		209,5	$7*10^6$-$23*10^6$
3%Ru/γ-Al_2O_3	(fresh)	179,1	$5,5*10^6$-$23,5*10^6$
	(spent)	149,9	$6*10^6$-$22,5*10^6$
3%Pd/γ-Al_2O_3	(fresh)	133,9	$5,5*10^6$-$26*10^6$
	(spent)	166,6	$5,5*10^6$-$22*10^6$
3%Pt/γ-Al_2O_3	(fresh)	168,9	$5*10^6$-$24,5*10^6$
	(spent)	138,8	$7*10^6$-$24*10^6$

coarsening of particles, while for palladium, on the contrary, the surface increases from 133.9 to 166.6 m^2/g. Micro and mesopores were found on the studied catalysts.

Conclusion

The catalysts are subjected to significant changes by conversion of a mixture of light alkanes in the range of 350 – 450 ° C and the following conclusions can be drawn:

- Particles on the surface are sintered and coarsened, which in platinum and ruthenium leads to a decrease in the specific surface area. In palladium, on the contrary, there is an increase in the specific surface area.
- Carbonization of the surface is observed on all spent catalysts.

The highest yield of olefins 10% is observed when a mixture of light alkanes with water is fed to the reduced catalyst at 3% Ru / Al_2O_3.

REFERENCES

1. Sokolsky D. V. *Gidrirovaniye v rastvorakh* [Hydrogenation in solutions]. Alma-Ata, 1962. 478 p.
2. Krylov O.N., Shub B.R. *Neravnovesnye protsessy v katalize* [Non-equilibrium processes in catalysis]. M.: Himija, 1990. 288 p.
3. Konuspayev S.R., Dosmagambetova I.B., Shengizbayeva A. B. *Alyumokhromovye i alyumoplatinovye katalizatory degidrirovaniya nizshikh parafinov* [Alumochromium and alumoplatinum catalysts of dehydrogenation of lower alkanes] // Chemical Journal of Kazakhstan. 2014. № 4(48). 61-71 p.
4. Shiyong Zhao, Bolian Xu, Lei Yu, Yining Fan. Catalytic dehydrogenation of propane to propylene over highly active PtSnNa / γ-Al_2O_3 catalyst // Chinese Chemical Letters. 2017. №29 (3). 475-478 p.
5. Zhanhua Ma, Yajing Mo, Jun Li, Changhua An, Xuenuan Liu. Optimization of PtSnK/Al_2O_3 isobutane dehydrogenation catalyst prepared by an impregnation-reduction method// Journal of Natural Gas Science and Engineering. 2015. №27. 1035-1042 p.
6. Lidan Deng, Hiroki Miura, Tetsuya Shishido, Zheng Wang, Saburo Hosokawa ,Kentaro Teramura, Tsunehiro Tanaka. Elucidating strong metal-support interactions in Pt–Sn/SiO_2 catalyst and its consequences for dehydrogenation of lower alkanes// Journal of Catalysis. 2018. №365. 277– 291 p.