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LAWS OF FORMATION OF ACTIVE AND SELECTIVE CATALYTIC SYSTEMS ON THE BASIS OF CLINOPTILOLITE FOR HEAVY HYDROCARBONS CRACKING PROCESS

Abstract. Using the modern physical methods (XPS, SEM, TEM, BET) regularities in the formation of catalytic systems based on clinoptilolite by the modification of various by nature acids were revealed. It is shown that as a result of interaction of the modifier with an active surface new structure is created, which lead to a significant increase in specific surface area and catalytic activity. A detailed study of the zeolite surface with TEM HR showed the formation of stable structures of clusters, which are partially embedded in the volume of the zeolite. The sizes of these clusters are 1-2 nm and are available for the reactants. It is believed that as a result of impregnating and calcining the catalytic systems, translation of heteropolyacid particles into highly dispersed state is achieved, where the heteropolyacid particles perform specific adsorption and catalytic properties.

Keywords: clinoptilolit, modification, texture, morphology, acidity, cracking catalytic systems.

Introduction. As an object of research work was natural zeolite from Shankanay region (Kazakhstan) in which the major rock-forming mineral is clinoptilolite, containing from 40 to 84 wt%. It is known, that zeolites being solid acids are basic catalysts of hydrocarbon cracking process [1, 2].

This paper presents the study of the acidic properties, the establishment of textural and morphological changes on the surface of clinoptilolite in the modification of it with different by nature acids or combination of them. We have previously reported that mineral acids carry out ions of alkali and alkaline earth metals from surface of natural zeolite; organic acids form soluble complex compounds with iron ions and mostly carry out ferric ions which catalyze the process of carbon formation from hydrocarbons; and additional modification of the zeolite by heteropolyacid leads to a deep loosening of its surface [3, 4].

EXPERIMENTAL PART

Catalytic systems based on natural Shankanay zeolite were created by modification with mineral, organic acids and heteropolyacids (HPA).

Changes in the composition and structure of the surface samples of natural zeolite in the acid treatment were followed by methods of spectral elemental analysis, BET, XPS, SEM, TEM, XRD and IR.

Oxide and elemental composition of samples of natural Shankanay zeolite was identified by emission-diffraction analysis on diffractometer DFS-13.

XRD analysis of catalytic systems was performed on D8 Advance (Bruker), α-Cu, tube voltage 40 kV, current 40 mA. Data processing and calculation of the diffraction patterns interplanar distances were performed using the software EVA. Deciphering trial and phase search were carried out under the program Search/Match with Database of powder diffractometric data PDF-2 Rel. 2012 (ICDD).

IR study of catalytic systems was conducted by the spectrometer NICCOLET-2700 in the frequency range 400-4400 cm^{-1}. The catalytic systems were formed into a tablet with "thickness" of 60-100 mg/cm^2. Adsorptions of test gases were carried out at different temperatures, vacuuming 10^{-5} Torr.

BET method by low-temperature nitrogen adsorption at the «AccuSorb» of «Mikromeitics» (USA) was used to identify specific surface area of catalytic systems.

By X-ray photoelectron spectroscopy (XPS) provided information on the qualitative and quantitative composition of the surface area of the test sample and the chemical state of elements. XPS- spectra were recorded on a photoelectron spectrometer ES-300 (KRATOS Analytical) in a mode of constant energy transmission energy analyzer photoelectrons, which is equipped with an automation system based on the IBM PC (held at the G.K. Boreskov Institute of Catalysis SB RAS, Novosibirsk). To capture, source of X-ray was used without monochromator. Radiation energy Mg Ka - was 1253.6 eV. The calibration of the energy scale was carried out on the binding energies of Au4f7/2 equal to 84.0 eV. Quality control of the chemical composition of the surface was carried out on the overview of the spectrum with a range of 0-1100 eV. For the analysis of the composition and chemical state of the elements were shooting narrow areas, and used mode: energy transmission spectrometer HV -25 eV step sweep - 0.1 eV.

C using scanning electron microscopy (SEM) with a spatial resolution of 1 and 10 Å microscope JSM-6X80 transmission and high resolution electron microscopy (TEM HR) microscope JEM-2010 by JEOL accelerating voltage of 200 kV and a resolution of 1,4 Å (0,14 nm) microfeatures and morphology of catalytic systems' surface, elemental composition of the observed point on the surface and the pattern of distribution of elements on the surface, as well as their dispersion were studied. By means of electron microscope Philips CM-20, equipped with EDAX-spectrometer microanalytical experiments were conducted (held at the G.K. Boreskov Institute of Catalysis SB RAS, Novosibirsk).

Using the IR method with low-temperature CO adsorption acidic properties of zeolite catalytic systems were studied [5]. Infrared spectra were recorded on FT-IR spectrometer FTIR-8300 Shimadzu 700-6000 cm^{-1} with resolution of 4 cm^{-1} and the number of scans equal to 100. IR spectra are reported in absorbance units referred to 1 g of catalytic systems per 1 cm^2 of the cross section of the luminous flux and are in units A/ρ, that means optical density A_ν at absorbance line ν normalized for tablet thickness sample r (in g/cm^2). Before recording spectra catalytic systems samples were compressed into tablets without binder. Samples of the catalytic systems were placed in a quartz cell for absorption measurement with windows from CaF_2, and trained on the vacuum adsorption unit under vacuum (p <10^{-6} bar) at 500 ^{0}C, 1 h.

RESULTS AND DISCUSSION

Investigation of textural characteristics of modified samples of natural zeolite. Table 1 shows the textural characteristics of catalytic systems obtained from a natural Shankanay zeolite modifyied by inorganic, organic, stepwise inorganic and organic acids, and stepwise inorganic acid and heteropolyacid: Kl – initial natural zeolite, HKl-1 – zeolite one time modified with a mineral acid, 10% H_4EDTA/Kl – natural zeolite modified with ethylenediaminetetraacetic acid, 10% H_4EDTA / HKl-1 – zeolite decationized with mineral acid and modified with ethylenediaminetetraacetic acid, 10% Hsal/HKl-1 – zeolite decationized with mineral acid and modified with sulfosalicylic acid, 10% PW_{12}-HPA/HKl-1 – decationized with mineral acid and modified with tungsten heteropolyacid of 12 series.

Table 1 – Textural characteristics of catalytic systems obtained
by modifying a natural zeolite of Shankanay field

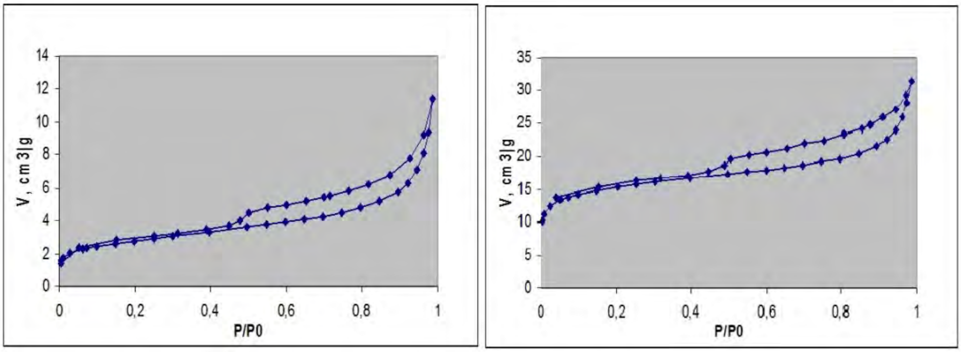
Samples	Specific surface area, m^2/g		Pore volumes, 10^{-3} cm^3/g		Pore size, A^o
	S	$S_{micropores}$	V	$V_{micropores}$	$D_{average}$
Kl	9,8	2,4	1,76	0,13 (7,4%)	72,2
10%H_4EDTA/Kl	28,2	–	–	–	–
HKl-1	52,6	38,0	4,86	0,18 (3,7%)	27,7
10%H_4EDTA/HKl-1	99,4	–	–	–	–
HSal/HKl-1	78,2	67,8	5,49	3,18 (58,0%)	21,2
10%PW_{12}-HPA/HKl-1	257,0	–	–	–	–

The total specific surface of the initial natural Shankanay zeolite is low and ranges of 9.8-22.1 m^2/g (table 1).

After modification specific surface area of the zeolite increases. For example, the specific surface area of clinoptilolite decationized by 1.75N hydrochloric acid increases up to 52,6-59,0 m^2/g, and the modification of a natural zeolite with ethylenediaminetetraacetic acid slightly increases the surface to 28.2 m^2/g (table 1).

Interesting results are obtained by modifying already decationized zeolite. Since the modification with EDTA leads to an increase in the specific surface area to 99.4, with sulfosalicylic acid up to 100.7 m^2/g, and the modification with HPA leads to an anomalous increase up to 257.0 m^2/g.

In figure 1 the adsorption and desorption isotherms of the natural clinoptilolite sample and its modified forms, which are characterized by the presence in



a)

b)

c)

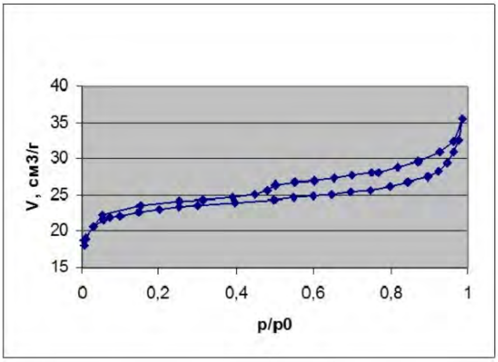


Figure 1 – Adsorption and desorption isotherms of natural clinoptilolite samples Kl (a) HKl-1 (b) and HSal/HKl-1 (c)

all sorption isotherms hysteresis S-shaped type are shown. Sorption hysteresis formed by the capillary condensation of gases and its location usually depends on the method of the modification.

The pore volume after modification initial zeolite by mineral acid increases from $1.76 \cdot 10^{-3}$ to $4.86 \cdot 10^{-3}$ cm^3/g, and until $5.49 \cdot 10^{-3}$ cm^3/g it is modified by sulfosalicylic acid. This increases relate not only the pore volume, but also increases its number from 7.4% in initial to 58.0% on zeolite modified sulfasalicylic acid (table 1).

In general increasing the number and volume of pores of the modified zeolite average pore size decreases. The average pore size of the initial zeolite is at 72.2 angstroms, hydrochloric acid modification is at 27.7, while for acid modification sulfasalicylic acid reduced to 21.2 angstroms (table 1).

The studies of the surface-modified natural zeolite samples by XPS. Using photoelectron spectrometer ES-300 received XPS-spectra of initial clinoptilolite and its modified forms: Kl, HKl-1, H_4EDTA/HKl-1; HSal/HKl-1, PW_{12}-HPA/HKl-1 и PMo_{12}-HPA/HKl-1. A typical photoelectron spectrum of a sample H_4EDTA/HKl-1 corresponding peaks of consisting chemical elements is displayed (figure 2). Quantitative analysis of the composition performed on the basis of calculation of the integrated intensities of the corresponding narrow lines in the spectra of XPS. Correction to the atomic sensitivity of each element of ASF was made.

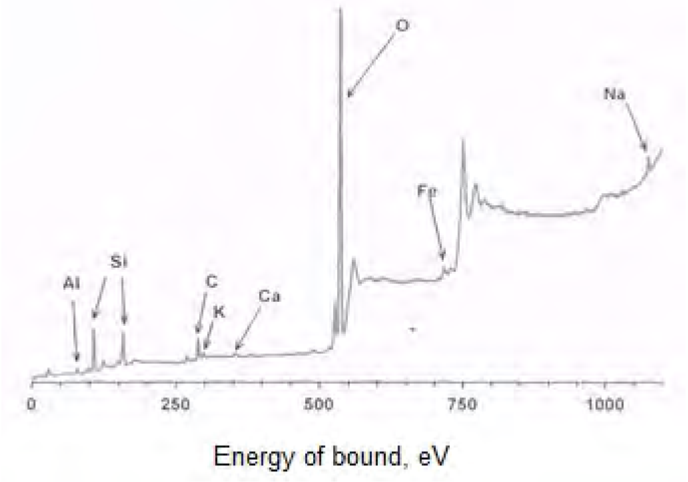


Figure 2 – Photoelectron spectrum of a sample H4EDTA/HKl-1

It can be seen that the sample contains aluminum, silicon, carbon, oxygen, also there is a small amount of potassium, calcium, and iron. These elements are part of almost all samples in this series. Silicon Si2p and aluminum A12p are presented as peaks with the characteristic binding energy of silicon and aluminum in the composition of zeolites and aluminosilicates. The peaks in the 750-1100 eV are due to the Auger process (electron emission from the outer shell during the process of relaxation after photoionization) and respectively belong to oxygen and carbon. Table 2 shows the elemental content calculated by XPS data normalized by the amount of aluminum.

Table 2 – The chemical composition of the surface of clinoptilolite samples

Sample	Al	Si	C	K	O	Fe	Ca	Na	W	Mo
Kl	1	3,0	4,4	0,08	16,8	0,19	0,30			
HKl-1	1	3,7	5,0	0,19	20,4	0,21	0,15			
H_4EDTA/HKl-1	1	5,4	5,3	0,16	25,9	0,31	0,13	0,26		
HSal/ HKl-1	1	7,3	8,3	0,2	34,1	0,39	0,12	0,11		
PW_{12}-HPA/HKl-1	1	6,1	7,7	0,22	33,0	0,35			0,58	
PMo_{12}-HPA/HKl-1	1	6,5	8,4	0,19	34,8	0,32				0,85

It is also remarkable that impregnating HPA on the surface affect the condition of other elements. From table 2 it is seen that in these zeolite samples the ratio of Si/Al varies quite substantially - from 3 to 6.5. However, given their relatively low concentration, it can be assumed that the change in the state of A1 and Si is mainly due to the mutual influence.

XPS spectra of samples PW_{12}-HPA/HKl-1 and PMo_{12}-HPA/HKl-1 showed the presence of tungsten and molybdenum (figure 3). In the original spectrum two doublets W4f with binding energies of the components $W4f_{7/2}$ 34.4 and 36.1 eV could be identified (figure 3a).

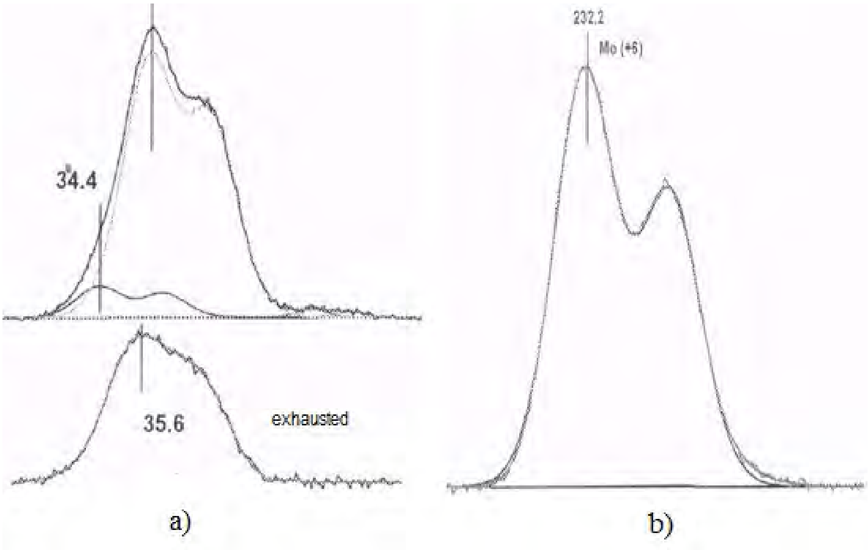


Figure 3 – Spectra of tungsten W4f (a) and molybdenum Mo3d (b)

Such binding energies are characteristic of the oxidized state of tungsten W^{3+} and W^{6+}, respectively. After the reaction only blurred doublet with a binding energy of the first component ~ 35.6 eV is observed, this is also related to the state of W^{6+}. Noticeable broadening of peaks may be due to structural inhomogeneity of HPA after exposure of reaction medium, or the formation of carbon on the surface and its effect on the HPA. The spectrum of molybdenum (figure 3b) can be approximated by only one doublet with a binding energy of component $Mo3d_{5/2}$ equal to 232.2 eV. Such binding energy is characteristic of the charged state of molybdenum (Mo^{+6}).

Thus, the XPS method makes it possible to evaluate energy state of surface elements, which makes it possible to understand the mechanism of action of the active center of the catalytic systems.

The studies of the surface conditions of modified natural zeolite samples by electron microscopy (TEM and SEM). Photographs of various modified natural zeolite samples which were obtained using a scanning electron microscope JSM-6X80 are shown on figure 4.

According to electronic images of natural zeolite granules are irregular in shape (figure 4, a) and are characterized by a specific structure consisting of irregularities and cracks, which causes the penetration of relatively large cations (figure 4, b).

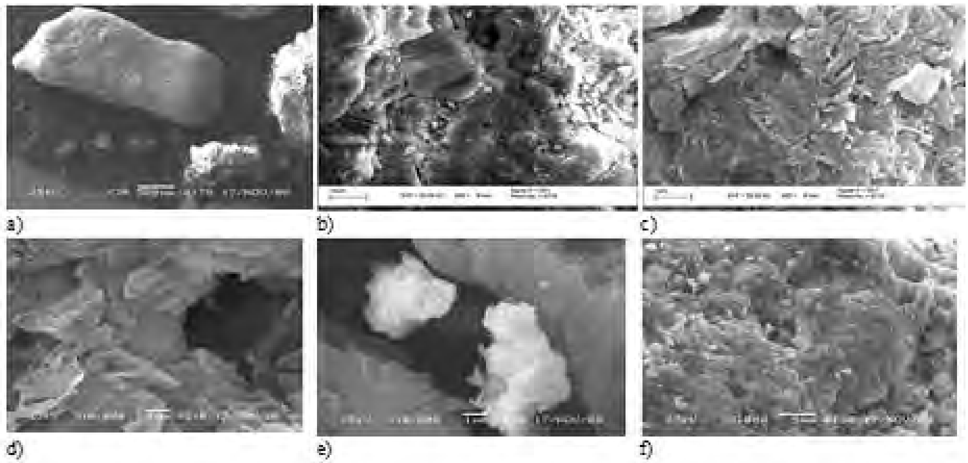


Figure 4 – An electron-microscopic photographs of identified samples of natural zeolite: natural zeolite granules (a) and its outer layer (b); HKl-1 (c); HSal/HKl-1 (d); PW_{12}-ГПК/НКл-1(e, f)

Surface of decationized clinoptilolite HKl-1, obtained by means of SEM, characterized by inhomogeneity and the presence of multiple shallow channels, which have a layered structure (figure 4, c).

When stepwise modifying with mineral acid as the first step then with organic acid, surface microfeatures are precise and nature of recesses of decationized clinoptilolite layered structures increases, the surface is even more loosened; particularly when modified with sulfosalicylic acid large pores appear and the surface is loosened with peeling whole layers and new pores appear (figuref 4, d). Microelement analysis data indicate that the ratio of clinoptilolite basic elements, in particular silicon to aluminum compared with the data of catalytic systems HKl-1 decreases. Wherein the catalytic systems surface HSal/HKl-1 low iron content was detected.

On figure 4 also photographs of the sample PW_{12}-HPA/HKl-1 are shown. It can be seen that the surface of clinoptilolite layered structures HKl after modification are covered with agglomerates of PW_{12}-HPA, that are evenly distributed and strongly bounded to the surface of clinoptilolite (figure 4, e, f).

In electron-microscopic images of a thin layer of catalytic systems PW_{12}-HPA/HKl-1 obtained by TEM microscope JEM-2010, the spots of different sizes, which have different shapes and contrasts are seen (figure 5). Microanalytical experiments on EDAX-spectrometer showed that the above mentioned spots have the same composition identical with the PW_{12}-HPA (figure 5).

Apparently, this is due to the high degree of dispersion and particle distribution of PW_{12}-HPA on the surface of clinoptilolite. The quality and quantity of the working surface could be mediated from that. Since, the observed point in the surface of the catalytic systems is composed of silicon (1.61%), aluminium (0.74%), oxygen (80.2%), and also phosphorus (1.52%) and tungsten (15.85%)

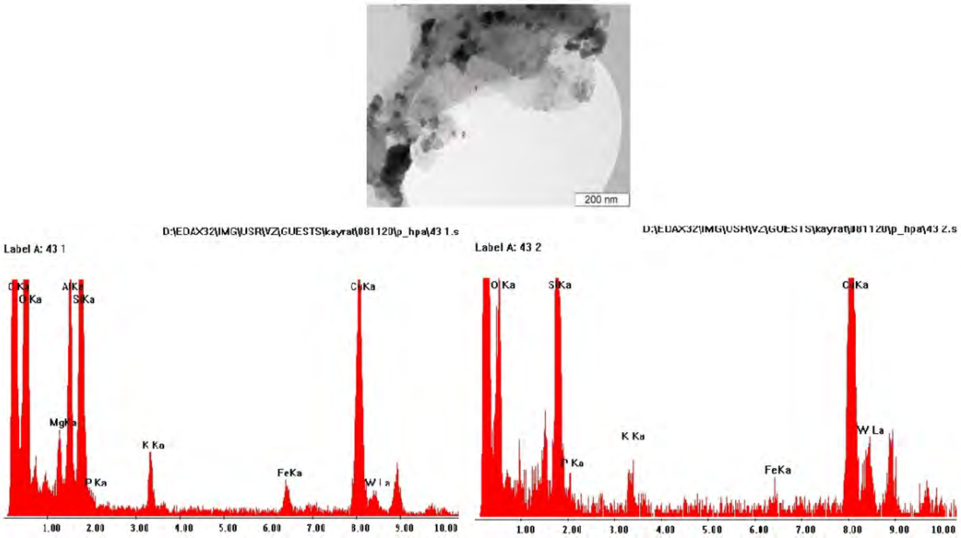


Figure 5 – An electron-microscopic image of the catalytic systems PW_{12}-HPA/HKl-1 obtained by TEM HR, a top under - X-ray spectra of the catalytic systems surface PW_{12} HPA/HKl-1 obtained from EDAX-spectrometer

are found which qualitatively correspond to the composition of the catalytic systems.

A detailed study of the zeolite surface by TEM HR, indeed, showed the formation of stable structures of clusters, which are partially embedded in the volume of zeolite (figure 6). The size of these clusters are 1-2 nm (figure 6). Often

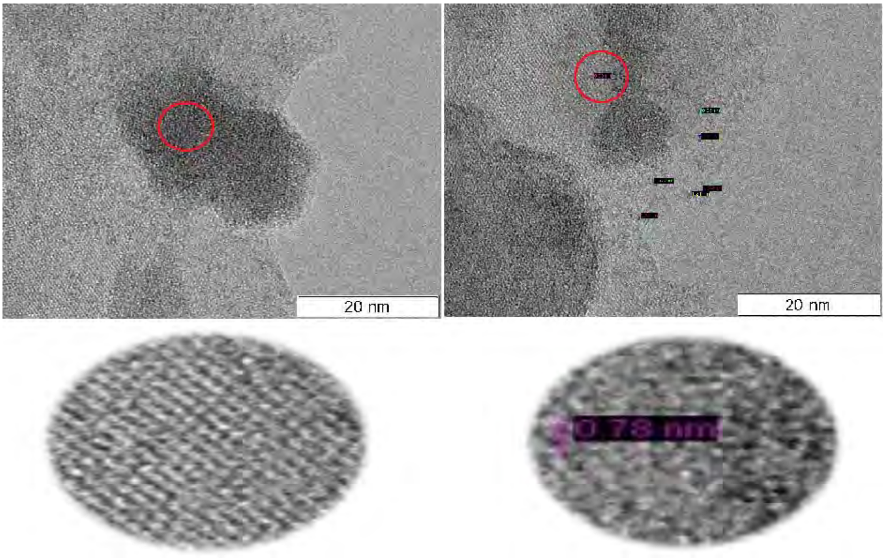
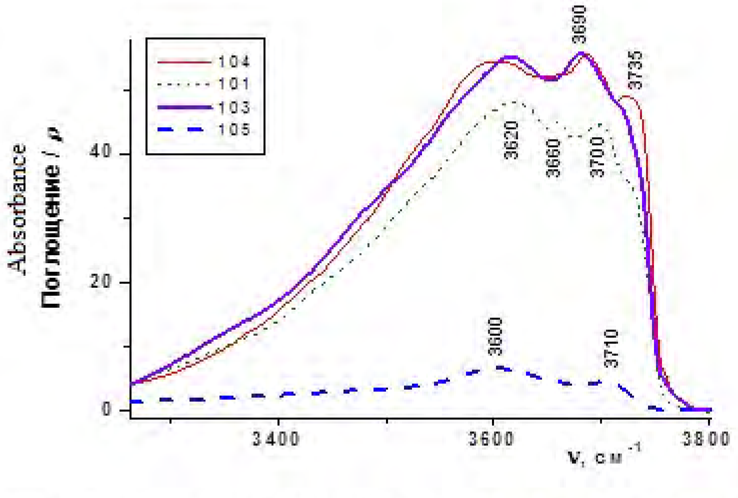


Figure 6 – Electron-microscopic images of the catalytic systems sample PW_{12}-HPA/HKl-1 obtained by TEM HR

occurring lines on images belongs to the clinoptilolite crystal lattice. Thus, clusters are uniformly distributed over the surface of the zeolite and are available for the reactants (figure 6).

In some places of the clinoptilolite surface highly dispersed particles of HPA are arranged as layers in the form of associates - in the pictures appear as a contrasting sites, at the same time the size of the particles clearly evident (0.78-1.32 nm) (figure 6). The compositions of nanostructures according to the EDAX-spectrometer are also identical with PW_{12}-HPA.

Investigation of the acidic properties of surface of modified natural zeolite samples. On the FT-IR spectrometer FTIR-8300 Shimadzu in the 700-6000 cm^{-1} field with a resolution of 4 cm^{-1} and the number of scans of 100 infrared spectra of catalytic systems were recorded; catalytic systems: HKl-1 (spectrum #104), 10% HSal/HKl-1 (spectrum #103), 10% H_4EDTA/HKl-1 (spectrum #105), 10% PW_{12}-HPA/HKl-1 (spectrum #101), obtained by modifying clinoptilolite samples with 1,75N hydrochloric, 10% sulfosalicylic, 10% ethylenediaminetetraacetic acid and 10% aqueous solution of tungsten of 12 row heteropolyacid ($H_3PMo_{12}O_{40}\cdot nH_2O$) respectively. Their IR spectra in the region of the stretching vibrations of OH groups, obtained by tests using the sequential adsorption of CO at the temperature 77K are shown in figure 7.



#104 - HK1; #101 - 10%PW12HPA/HK1; #103 - 10%HSal/HK1; #105 - H4EDTA/HK1

Figure 7 – IR spectra of catalytic systems samples in the region of OH groups' stretching vibrations

In the spectrum of the sample 10%PW_{12}-HPA/HKl peaks related to the absorption of the isolated OH groups at 3620, 3660, 3700 and 3735 cm^{-1} are observed. In the spectrum of the samples HKl and 10%HSal/HKl an increase in the intensity of isolated OH groups peaks as compared with a sample of 10%PW_{12}-HPA/HKl is observed, that may indicate a slight increase in the concentration of hydroxyl-cover. For samples HKl and 10%HSal/HKl compared with a sample of 10%PW_{12}-HPA/HKl the appearance of intense broad peak at 3680-3690 cm^{-1} is observed. For a sample of 10%HSal/HKl compared with a sample of 10%PW_{12}-HPA/HKl observed shifting of isolated groups to the low-frequency region (3620→3600 cm^{-1}), and a significant increase in the intensity of 3735 cm^{-1} region. The sample 10%H_4EDTA/HKl, assumed to have destroyed zeolite structure, in the spectrum of this sample low intense broad peaks at 3600 and 3710 cm^{-1} are observed. The total concentration of OH groups to sample 10%H_4EDTA/HKl, referred to the sample weight was 8-10 times lower than for the other samples.

Strength of Broensted acid sites can be determined from the magnitude of the shift of the stretching vibrations of OH groups ($\Delta\nu_{OH}^{CO}$) in the presence of adsorbed CO. The greater the shift, the stronger acidic sites. Concentration of Broensted acid sites and their strength, expressed in terms of wavenumber shift amount shown in table 3.

Table 3 – Broensted acid sites (B.a.s.) and their concentration
on the surface of hydrocarbons cracking catalytic systems

Catalytic system	SiO_2/Al_2O_3	B.a.s. I		B.a.s. II		B.a.s. III	
		$\Delta\gamma_{OH}$, cm^{-1}	C, μmol/g	$\Delta\gamma_{OH}$, cm^{-1}	C, μmol/g	$\Delta\gamma_{OH}$, sm^{-1}	C, μmol/g
10%PW_{12}-HPA/HKl		340	4	320	6	220	30
HKl	23,6	340	4	280	20	225	45
10%HSal/ HKl	12,6	340	1	310	15	235	35
10%H_4EDTA/ HKl	19,4	–	–	–	–	–	–

Thus, there are three types of the acidic centers on samples of catalytic systems that differ in strength and concentration, which is determined by the magnitude and intensity of the shift. When the adsorption of CO on the catalytic systems the greater the shift of the OH groups' stretching vibrations (ΔγOH, cm^{-1}), the stronger the acid sites. Strong acid sites are found on 10%PW_{12}-HPA/HKl and HKl. On 10% HSal/HKl their concentration is 4 times lower, and on 10% H_4EDTA/HKl shift is not observed, giving rise to talk about the absence of surface Brönsted acid sites.

Bronsted sites of the second type on 10% PW_{12}-HPA/HKl stronger by the shift than on the other catalytic systems, although the concentration is less. Acid sites of the third type on the catalytic systems approximately the same amount, but they apparently do not determine the activity when cracking. The total concentration of strong acid sites on 10%PW_{12}-HPA/HKl is greater than on the other catalytic systems samples.

Discussions. Modification of natural zeolite sample with various acids leads to structural changes of clinoptilolite. Acid activation of clinoptilolite increases its surface and pore volume, decreases average pore diameter, which in turn directly affect the properties of the active acid sites of the zeolite, which are responsible for acid-base reactions, as well as their distribution on the catalytic systems surface.

The study found that the catalytic systems obtained by modification of natural zeolite with various substances, by the specific surface area, starting from the lowest arranged in a row:

Kl → H4EDTA/Kl → HKl-1 → H4EDTA/HKl-1 →
→ HSal/HKl-1 → PW12-HPA/HKl-1

Special attention deserves the significant growth of the surface when the modification with 10% PW12-HPA to 257.0 m^2/g, since this value is much higher than for pure zeolite and HPA. Obviously, when HPA applied on the surface of the zeolite there is a deep interaction occurs. In addition, this increase is due to the formation of new nanostructures that have been shown by TEM and SEM.

In a row of samples:

Kl → HKl-1 → HSal/HKl-1

area of hysteresis loop decreases and the amount of gas adsorbed on the surface of clinoptilolite increases. This fact can be attributed to an increase in pore volumes of the samples. By volume of pores the catalytic systems starting from the lowest may be arranged in a row:

Kl → HKl-1 → HSal/HKl-1

The pore distribution on the samples of catalytic systems surface shifts toward micropores, or in other words, on the surface mainly micropores are found.

Obviously, the surface growth of the samples of catalytic systems is due to the formation of new micropores. Determination of surface micropores (S_{mc}) also shows their growth from 2.49 to 38.07 m^2/g after modification with hydrochloric acid and to 67.84 m^2/g with sulfosalicylic acid.

Using the method of XPS information about the qualitative and quantitative composition of the surface area of the samples and the chemical state of elements was obtained. Since the samples were subjected to severe impacts of acid there might be amorphization of their surfaces. Applying HPA on the surface affect the condition of the other elements. However, given their relatively low concentration, it can be assumed that the change in the state of A1 and Si is mainly due to the mutual influence. At the same time, purely qualitatively it can be concluded that the decrease in binding energy due to the transition A12p of aluminosilicate type structures to aluminum rich structures. This is also supported by earlier data of IR and XRD.

As a result of the XPS study it was found that when impregnating heteropolyacids of molybdenum and tungsten series, the zeolite framework partially decomposed with the formation of individual and Al-O- and Si-O- structures. Since conditions of the main elements of the zeolite varies a little. Molybdenum and tungsten in catalytic systems are in present as Mo (6+) and W (6+), respectively, which evidence of retaining heteropoly-like structure.

Morphology and microfeatures, elemental composition in the observed point ,the distribution pattern of elements on the surface of initial clinoptilolite and its acid-modified forms examined by electron microscopy.

Thus, in particular, using an SEM indicated that after step-modifying by mineral acid then heteropolyacid, heteropolyacid particle dispersion on the surface of the zeolite are high; the layered structure of the zeolite covered with uniformly distributed and tightly bounded to its surface a heteropolyacid agglomerates.

When modification of zeolite with decationized HPA of Tungsten 12 series, as already mentioned above, there is a sharp increase in the specific surface area of the catalytic systems. Obviously, when HPA impregnated on the surface of the zeolite there is a deep interaction. Thus on the TEM HR images of catalytic systems homogeneous structures of HPA interspersed into the pores of the zeolite are visible. The dimensions of these structures are a few nanometers. Obviously, the occurrence of these nanostructures alters the catalytic properties, particularly cracking activity of the catalytic systems considerably increases, consequently the yield of liquid products of the cracking reaction, constituting mainly of the long-chain α-olefins increase.

By means of CO adsorption method of strength and concentration of acid sites of the samples of catalytic systems were identified. In the series starting from lowest:

$$\text{HKl} \rightarrow 10\%\text{HSal/HKl} \rightarrow 10\%\ \text{PW}_{12}\text{-HPA/HKl}$$

there is a significant increase in the proportion of strong and very strong Bronsted acid sites. The total concentration of strong acid sites on 10%PW_{12}-HPA/HKl and sum of shifts at 340 cm^{-1} and 320 cm^{-1} is higher than on HKl. It should be noted that the increase in acidity correlates with high silicate modulus (SiO_2/Al_2O_3) of the zeolite sample.

Conclusions. Thus it is clear that the occurrence of nanostructures and the large number of strong acid sites leads to increase of cracking activity catalyst systems based on clinoptilolite in the cracking of heavy hydrocarbons.

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Резюме

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АУЫР КӨМІРСУТЕКТЕРДІ КРЕКИНГЛЕУ ПРОЦЕСТЕРІНІҢ КЛИНОПТИЛОЛИТ НЕГІЗІНДЕГІ АКТИВТІ ЖӘНЕ СЕЛЕКТИВТІ КАТАЛИТИКАЛЫҚ ЖҮЙЕЛЕРІН ҚАЛЫПТАСТЫРУДЫҢ ЗАҢДЫЛЫҚТАРЫ

Заманауи физикалық әдістерді (РФЭС, СЭМ, ПЭМ, БЭТ) қолдана отырып ауыр көмірсутектерді крекинглеу процестерінің клиноптилолит негізіндегі активті және селективті каталитикалық жүйелерін оны табиғаты әртүрлі қышқылдармен модифицирлеу арқылы қалыптастырудың заңдылықтары анықталды. Модификаторлар мен клиноптилолиттің беткі қабатынының белсенді әрекеттесуінің нәтижесінде жаңа құрылымдар түзіліп, олардың каталитикалық жүйенің беткі қабаты ауданы мен каталитикалық активтілігін біршама өсіретіндігі көрсетілді. Модификатор ретінде гетерополиқышқылдар қолданылған жағдайдағы цеолит бетін кең шешімді ПЭМ әдісімен тиянақты зерттеу цеолиттің ішкі көлеміне жартылай енген қышқылдың тұрақты кластерлік құрылымдары түзілетіндігін айқындады. Бұл кластерлердің өлшемдері 1-2 нанометр құрайды және олар әрекеттесуші реагенттерге қолжетімді. Модификатор ретінде гетерополиқышқылдарды цеолитке отырғызып және алынған катализаторлық жүйені қыздырып шынықтырғанда гетерополиқышқыл бөлшектері жоғары дисперсті күйге ауысады, соның нәтижесінде олар ерекше адсорбциялық әрі каталитикалық қасиеттер көрсетеді деп қорытынды жасалды.

Түйін сөздер: табиғи цеолит, модифицирлеу, текстура, морфология, қышқылдық, крекинг катализаторлары.

Резюме

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ЗАКОНОМЕРНОСТИ ФОРМИРОВАНИЯ АКТИВНЫХ И СЕЛЕКТИВНЫХ КАТАЛИТИЧЕСКИХ СИСТЕМ НА ОСНОВЕ КЛИНОПТИЛОЛИТА ДЛЯ ПРОЦЕССОВ КРЕКИНГА ТЯЖЕЛЫХ УГЛЕВОДОРОДОВ

С применением современных физических методов (РФЭС, СЭМ, ПЭМ, БЭТ) выявлены закономерности формирования каталитических систем на основе клиноптилолита для процессов крекинга углеводородов при модифицировании их различными по природе кислотами. Показано, что в результате активного взаимодействия модификаторов с поверхностью образуются новые структуры, которые ведут к значительному росту удельной поверхности и каталитической активности. Детальное изучение поверхности цеолита методом ПЭМ ВР показало образование устойчивых структур кластеров, которые частично внедрены в объем цеолита. Размеры этих кластеров составляют 1-2 нанометров и они доступны для реагирующих веществ. Считается, что при нанесении и в результате прокаливания катализатора достигается перевод частиц гетерополикислоты в высокодисперсное состояние, при котором у частиц гетерополикислоты появляются особые адсорбционные и каталитические свойства.

Ключевые слова: природный цеолит, модифицирование, текстура, морфология, кислотность, катализаторы крекинга.