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## CATALYSTS OF CRACKING ON THE BASIS OF HETEROPOLYACIDS

**Abstract.** Heteropolyacids (HPA) are strong Bronsted acids. The heteropolyacids of the 12 series the most value for catalytic reactions are. The purpose of the work was to develop the composition of cracking catalysts based on the natural zeolite of the Shankanay deposit (Kazakhstan). Modification of the catalysts was carried out with mineral acids, organic acids and HPA. The catalysts have been extensively studied by a complex of physicochemical methods. According to IR spectroscopy data, after decationation and dealumination, the natural zeolite does not change its crystal structure. Presumably, the formation of the bond of HPA with the zeolite occurs when the zeolite of the HPA is modified. Electron microscopy data indicate high degrees of dispersion and particle distribution of PW<sub>12</sub>-HPA on the surface of clinoptilolite. A detailed study of the zeolite surface by the TEM-BP method has shown the formation of stable cluster structures 1-2 nm in size, which are partially embedded in the zeolite volume. These clusters are evenly distributed over the surface of the zeolite and are available for reacting substances.

**Keywords:** catalytic cracking, heteropolyacids, zeolite of the Shankanay deposit, electron microscopy.

### Introduction

Catalysis using heteropolycompounds is one of the important directions in modern catalysis. In acid catalysis, predominantly heteropolyacids are used. The compounds of a proton with a complex anion of inorganic polyoxometallates - molybdenum, tungsten, less frequently vanadium are called heteropolyacids (HPA) [1-3]. HPA are ionic crystals in the solid state, they consist of a large heteropolyanion, a cation, crystallization water, in some cases they also contain additional molecules. The unique physicochemical properties of HPA, providing great potential for the preparation of catalysts with controlled acidity, dispersity of the modifier metal, increased thermal stability, have led to their use as modifiers of heterogeneous catalysts in catalysis<sup>7-11</sup>. The highest value for catalysis is HPA of 12 row. They contain heteropolyanions - the structures of the most common heteropolyanion Keggin  $X^xM_{12}^{vi}O_{40}^{x-8}$  or  $X^xM_{12-n}^{vi}O_{40}^{x-n-8}$ , where X is a central atom (Si<sup>vi</sup>, P<sup>v</sup>, As<sup>vi</sup>), x is its oxidation degree, M is metal (molybdenum, tungsten or vanadium)<sup>12-15</sup>. HPA of tungsten row PW<sub>12</sub>-HPA (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>•6H<sub>2</sub>O) or of molybdenum row PMo<sub>12</sub>-HPA (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>•6H<sub>2</sub>O) are well studied<sup>4-7, 16-19</sup>. In the Keggin anion H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, for example, the tungsten atom is located in the center of the oxygen octahedron. The phosphorus atom is surrounded by 12WO<sub>6</sub> octahedra, forming PO<sub>4</sub> tetrahedron. This structure is retained in concentrated solutions of HPA even after the loss of several oxygen atoms. For this reason, HPA has, like zeolites, a high adsorption capacity. For example, polar molecules such as water and alcohols easily penetrate the pores of the HPA and leave the volume of the catalyst, expanding and compressing the distances between the keggin anions, while nonpolar molecules (eg, hydrocarbons) do not give such an effect. This model allows to successfully explain the characteristic behavior of HPA, for example, high catalytic activity at low temperatures, the Keggin structure has a sufficiently high strength<sup>21</sup>. Acid-catalytic liquid-phase

processes based on HPA catalysts were carried out on an industrial scale, for example, hydration of propylene, isobutylene, butenes, polymerization of tetrahydrofuran<sup>22-26</sup>. HPA are strong Bronsted acids and surpass the strength of many mineral acids. HPA have stronger acid sites than the zeolites HX, HY and amorphous aluminosilicates. The acidity of the solid acidity of HPA close to acidity of superacids. This determines the prospects of their use as acidic homogeneous and heterogeneous catalysts. HPA can be applied to the surface of such carriers as SiO<sub>2</sub>, TiO<sub>2</sub>. The main carriers-Al<sub>2</sub>O<sub>3</sub>, MgO, - tend to decompose HPA. The practical use of HPA is mainly due to their use as catalysts for the oxidation of unsaturated hydrocarbons, olefin polymerization, epoxidation. Solid HPA, including applied, are used as catalysts in the alkylation of aromatic compounds, hydration of olefins and in other acid-type reactions. Heteropolycompounds of molybdenum find application as flame delayers<sup>27</sup>. An even wider area is their use in reactions where it is necessary to combine acid-base and oxidation-reduction properties of the catalyst<sup>28</sup>. It is known that the acid nature of the catalyst plays a fundamental role in the cracking of hydrocarbon feedstocks. However, the information on the use of HPA in cracking is not numerous, and the cracking properties of HPA-modified natural zeolites have not been practically investigated<sup>8, 29,30</sup>.

The aim of the work is the synthesis of cracking catalysts based on the natural zeolite of the Shankanay deposit (Kazakhstan), modified with mineral acids, organic acids and HPA and the study of the qualitative and quantitative compositions of the working surface of the catalysts by physical and chemical methods of investigation.

#### Materials and methods

For preparation of long-chain  $\alpha$ -olefins from paraffins, cracking catalysts based on the natural zeolite of the Shankanay deposit (Kazakhstan) were prepared by modifying the natural zeolite with mineral acids, organic acids and HPA. Samples were also synthesized on the basis of industrial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with bulk density 0.68 g/cm<sup>3</sup> modified by HPA. For removal various metals from the cation surface (mainly alkaline and alkaline earth), the zeolite was treated with mineral acids. Natural zeolite (NZ) and previously decationated with hydrochloric acid samples of natural zeolite (H-NZ) were processed with complexons. For example, using one-, two- and three-fold modification of the natural zeolite with 1.75 N HCl samples of cracking catalysts: H-NZ-1, H-NZ-2 and H-NZ-3 were synthesized. For the selective removal of Fe<sup>3+</sup> iron ions, facilitating the carburization process, a chosen zeolite was treated with organic acids. For this aim, chelating agents (for example, sulfosalicylic acid and citric acid with 10% or 20% concentration), ethylenediamine-tetraacetic acid and its disodium salt of EDTA (Trilon B, aqueous 10% strength solution) were used. All these listed compounds with iron ions form stable water-soluble complexonates.

Treatment of zeolites with HPA was carried out for strengthening of force of the acid centers on which cracking reaction proceeds. For this aim the new catalysts for the cracking of decationized natural zeolite and industrial aluminum oxide have been synthesized and have been modified by the heteropolyacids of the molybdenum and tungsten series: PMo<sub>12</sub>-HPA/H-NZ, PMo<sub>12</sub>-HPA/Al<sub>2</sub>O<sub>3</sub>, PW<sub>12</sub>-HPA/H-NZ and PW<sub>12</sub>-HPA/Al<sub>2</sub>O<sub>3</sub>. HPA were used in an amount of 1.0% to 10% by impregnation on the surface of a decationized natural zeolite (H-NZ) by a known technique<sup>7,9,15,19</sup>.

#### Results and discussion

By IR spectroscopy and X-ray diffraction analysis were studied the structure and phase composition of the catalysts synthesized on the basis of the natural zeolite of the Shankanay deposit (NZ-1) and industrial alumina, modified by the HPA of the molybdenum and tungsten series (PW<sub>12</sub>-HPA/H-NZ-1 and PW<sub>12</sub>-HPA/Al<sub>2</sub>O<sub>3</sub> (the content of the HPA was 1%, 3%, 5%, and 10%), 10% of PMo<sub>12</sub>-HPA/H-NZ-1 and 10% of PMo<sub>12</sub>-HPA/Al<sub>2</sub>O<sub>3</sub>). The IR spectra (fig. 1, 2) of the starting PMo<sub>12</sub>-HPA and PW<sub>12</sub>-HPA contain the following main absorption bands: 510; 594; 789; 867; 962; 1,065; 1,400; 1,618; 2,850; 2,925; 3,210; 3,419 cm<sup>-1</sup>, which are typical for the compound of the composition H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> • 6H<sub>2</sub>O and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> • 6H<sub>2</sub>O, respectively (fig. 1, a; fig. 2, a). The results of the investigation of the samples of H-NZ-1, PMo<sub>12</sub>-HPA/H-NZ-1, PW<sub>12</sub>-HPA/H-NZ-1 by IR spectroscopy and their comparative analysis show that their spectra contain characteristic absorption bands of the clinoptilolite type zeolite in the region of 465; 615; 780; 1,060; 1,635; 3,460 cm<sup>-1</sup>. In the IR spectra of the zeolite sample of the Shankanay field activated by acid, these absorption bands are very clearly manifested (fig. 1, b, c; fig. 2b, c); at decationization and dealumination, the natural zeolite retains its crystalline structure. Figures 1, 2 show that the modification of the HPC of an acid-activated sample of zeolite of the Shankanay deposit is unambiguously manifested in the IR spectra of the resulting catalysts. For example, when PMo<sub>12</sub>-HPA is introduced into the zeolite

composition on the IR spectra of the catalyst, some absorption bands characteristic of zeolites are shifted and new bands appear.

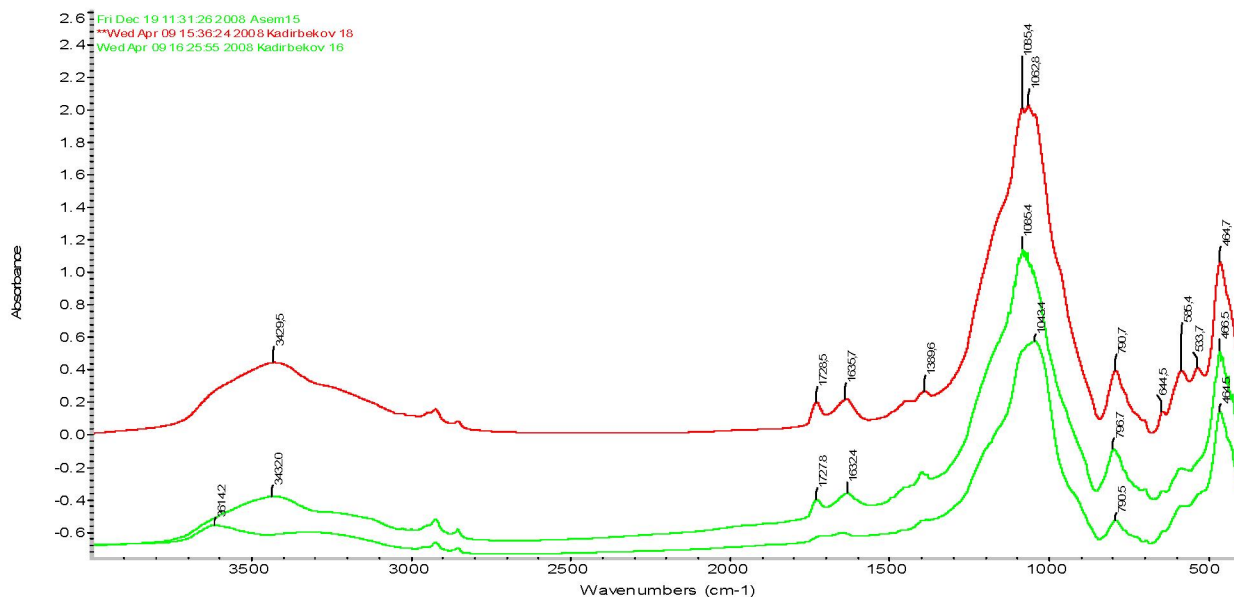


Figure 1-IR spectra of the catalyst 10%  $PW_{12}$ -HPA/H-NZ-1 and its components:  
 a) lower green curve- initial tungsten HPA -  $PW_{12}$ -HPA ( $H_3PW_{12}O_{40} \cdot 6H_2O$ ),  
 b) upper green curve - H-NZ-1, c) red curve - the catalyst 10%  $PW_{12}$ -HPA/H-NZ-1

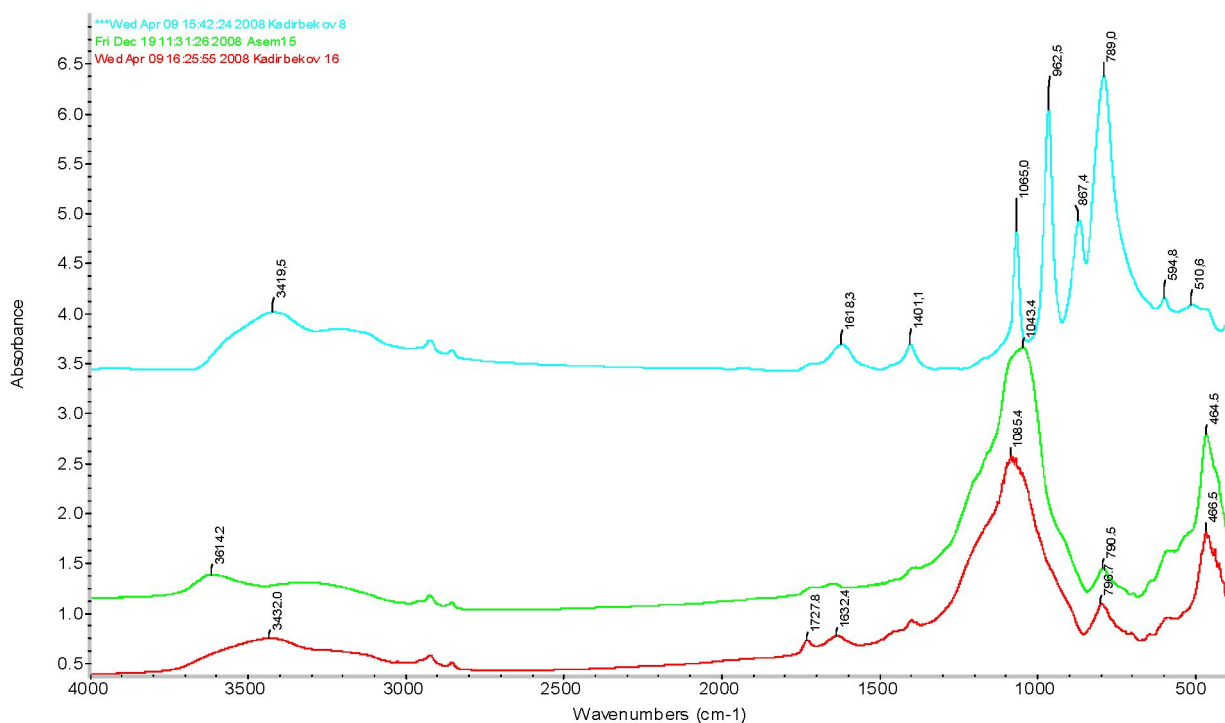
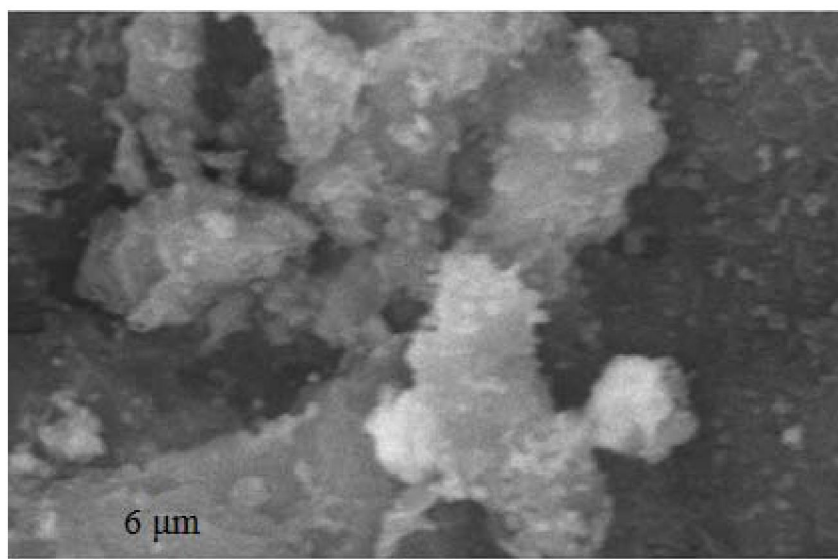


Figure 2-IR spectra of the catalyst 10%  $PMo_{12}$ -HPA/H-NZ-1 and its components:  
 a) red curve- initial molybdenum HPA- $PMo_{12}$ -HPA ( $H_3PMo_{12}O_{40} \cdot 6H_2O$ ),  
 b) green curve- H-NZ-1, c) blue curve - 10%  $PMo_{12}$ -HPA/H-NZ-1 catalyst

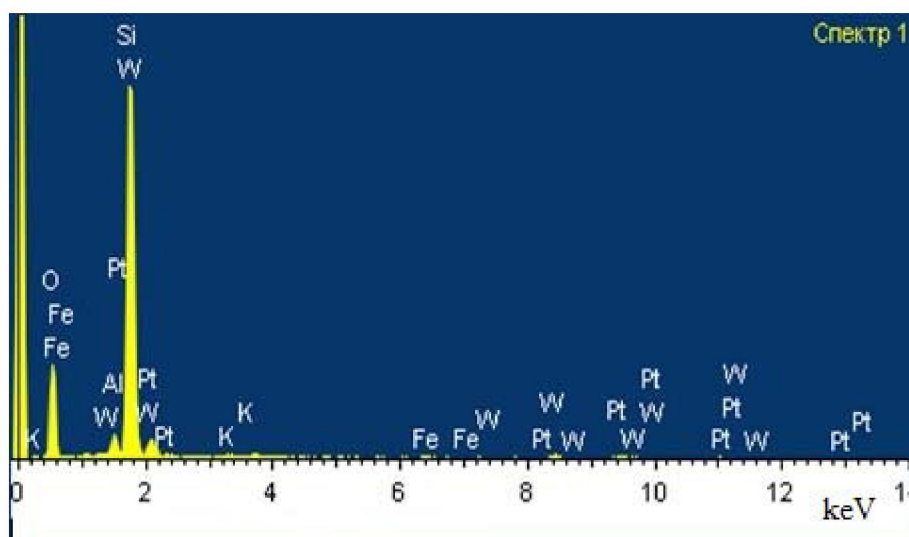
So, a shift of the band in the region of  $1,060\text{ cm}^{-1}$  to  $1,097\text{ cm}^{-1}$  and  $1,108\text{ cm}^{-1}$  is found. The absorption band of  $780\text{ cm}^{-1}$  disappears, and in the  $800\text{ cm}^{-1}$  area a new band appears, which is typical for

valence vibrations of the Si-O bond. This indicates the formation of a bond of HPA with a zeolite. If take into account the appearance of a shift in the band in the range of 1,065 to 1,100  $\text{cm}^{-1}$ , it can be concluded that Al-O-Si-bonds are broken in the zeolite structure and Si-O-Si bonds are formed, and aluminum goes into the ion exchange position. Dealumination of the clinoptilolite framework is also indicated by the appearance and growth of the intensity of the shoulder at 1,210  $\text{cm}^{-1}$  on the IR spectra of this sample, referring to the asymmetric valence vibrations of the Si-O end groups. In spite of it a complete destruction of the crystalline skeleton of the zeolite is not revealed and only its partial amorphization is observed.

The EM-image and the elemental composition of the scanned section of the catalyst  $\text{PW}_{12}$ -HPA/H-NZ-1 (fig.3) show that the content of its basic elements predominates on the surface of the zeolite, at the same time, the intensities of the spectra of the components of the HPA (tungsten and phosphorus) are clearly manifested. Apparently, this is due to the high degrees of dispersion and distribution of  $\text{PW}_{12}$ -HPA particles over the surface of clinoptilolite.



a



b

Figure 3- Electron microscopic image(a) and elemental composition (b) of the scanned section of the catalyst  $\text{PW}_{12}$ -HPA/H-NZ-1, obtained by SEM



X-ray patterns of the samples also indicate a change in the structure of the natural zeolite when modifying its by HPA (fig.4). Thus, a decrease in the intensity of one of the main peaks and the disappearance of several peaks characteristic of the mineral clinoptilolite on X-ray patterns of 10%  $\text{PMo}_{12}$ -HPA/ H-NZ-1 and 10%  $\text{PW}_{12}$ -HPA / H-NZ-1 were clearly detected, which is apparently related to partial amorphization of the structure and a change in the cation composition of the zeolite surface.

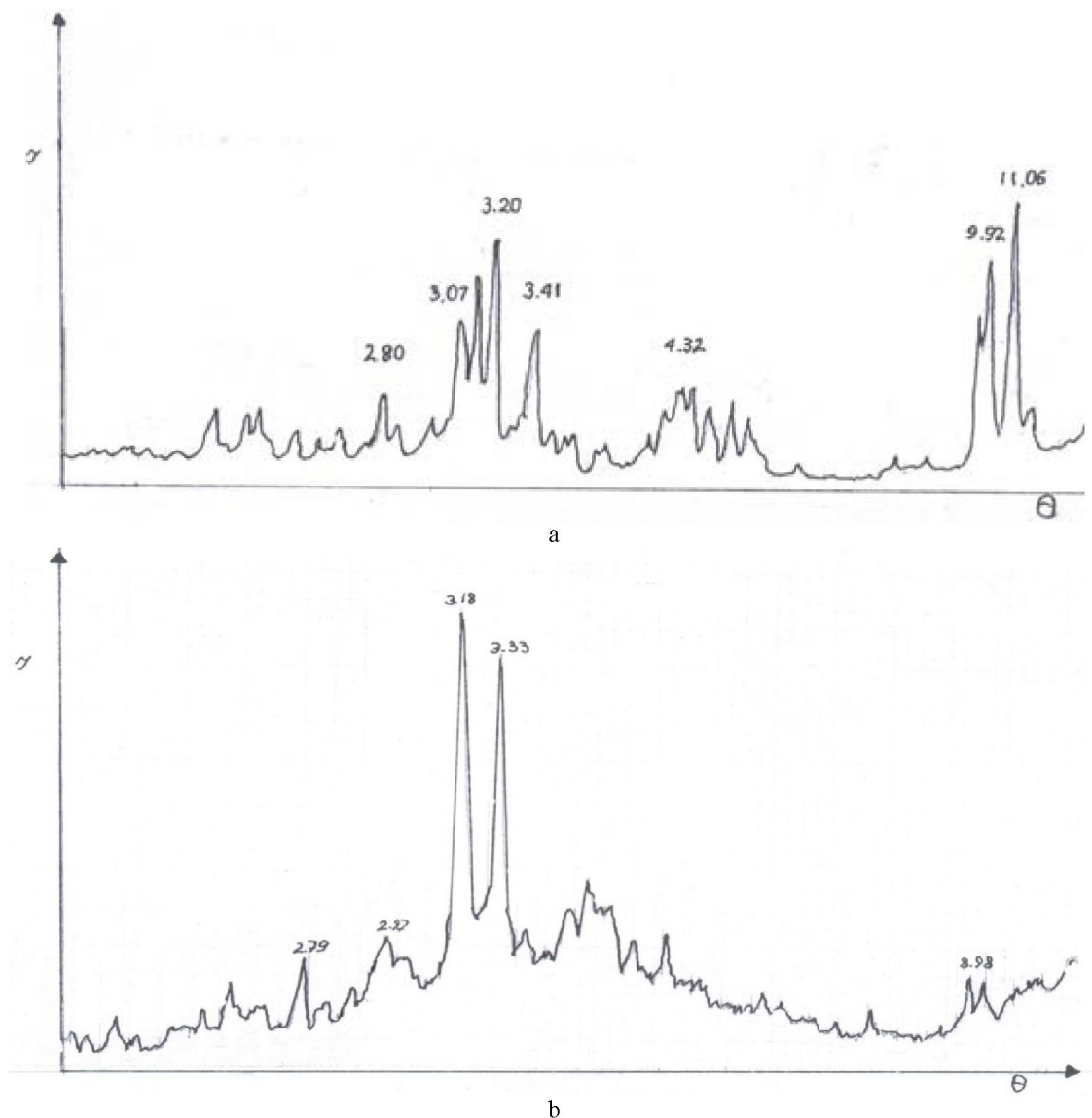


Figure 4 - The XRD pattern of the catalyst 10%  $\text{PMo}_{12}$ -HPA / H-NZ-1:  
 a) X-ray diffraction pattern of the initial HPA:  $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ ,  
 b) X-ray diffraction pattern of the catalyst 10%  $\text{PMo}_{12}$ -HPA / H-NZ-1

It was found in electron microscopic images of a thin layer of catalyst  $\text{PW}_{12}$ -HPA/H-NZ-1, obtained by TEM (translucent electronic microscopy), it is possible to see spots of different sizes with different shapes and contrasts. The microanalytical experiments on the EDAX-spectrometer showed that the above-mentioned spots have the similar compositions, identical to the  $\text{PW}_{12}$ -HPA (fig. 5).

It is considered<sup>11, 20, 24, 29</sup> that during the deposition and as a result of calcination of the catalyst,  $\text{PW}_{12}$ -HPA is converted to a highly dispersed state, in which  $\text{PW}_{12}$ -HPA particles exhibit special adsorption and catalytic properties. It is obvious that the emergence of nanostructures and the presence of a large number of strong acidic centers lead to an increase in the cracking activity of the catalyst of 10%  $\text{PW}_{12}$ -HPA/H-NZ during the cracking of paraffins.

A detailed study of the zeolite surface by the TEM-BP method has shown the formation of stable cluster structures 1-2 nm in a size, which are partially embedded in the zeolite volume (fig.5). These clusters are evenly distributed over the surface of the zeolite and are available for reacting substances.

In some places on the surface of clinoptilolite, the fine particles of the HPA are located in layers in the form of associates - they appear in the images as contra-sections, while the particle sizes clearly appear (0.78 - 1.32 nm) (fig. 6). Compositions of nanostructures according to the EDX-spectrometer are also identical with  $PW_{12}$ -HPA.

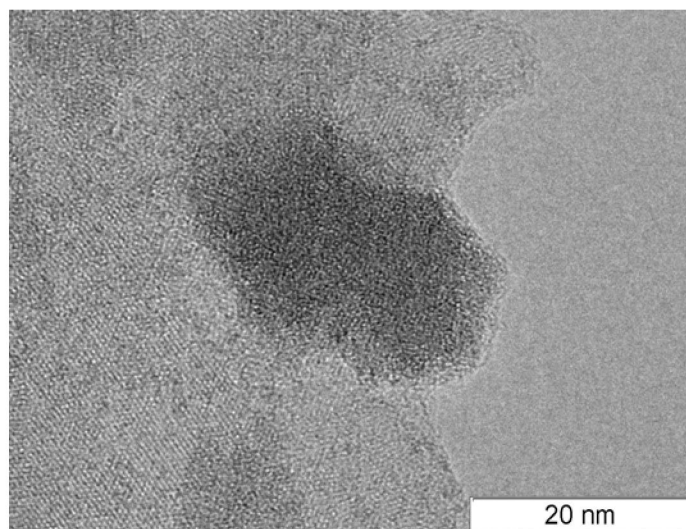


Figure 5 - Electron microscopic image of the catalyst  $PW_{12}$ -HPA / H-NZ-1, obtained by TEM BP.  
Degree of resolution 1cm = 20nm

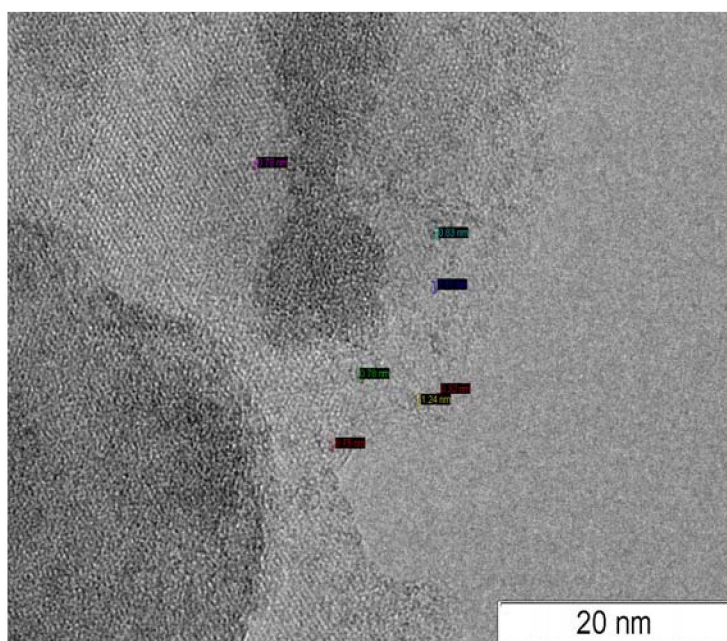


Figure 6- Electron microscopic image of the catalyst  $PW_{12}$ -HPA / H-NZ-1, obtained by the TEM-BP method.  
Degree of resolution 1cm = 20nm

### Conclusion

In the work catalysts for cracking on the basis of natural zeolite of the Shankanay field (Kazakhstan) modified by mineral acids, organic acids and HPA were synthesized. Investigations of the working surface of catalysts by physical and chemical methods of a research were carried out. By IR data during

decathionization and dealumination the natural zeolite retains its crystalline structure. It is possible to assume formation of a bond of HPA with a zeolite at modifying of the zeolite by HPA. Possibly because of the shift of the band in the region of 1,065 to 1,100  $\text{cm}^{-1}$  the Al-O-Si- bonds are broken in the zeolite structure and Si-O-Si- bonds are formed, and the aluminum goes into the ion exchange position. The complete destruction of the crystalline skeleton of the zeolite is not revealed, only partial amorphization is observed. X-ray patterns of the samples also indicate a change in the structure of the natural zeolite when its is modified by HPA. By EM data there are high degrees of dispersion and particle distribution of PW12-HPA on the surface of clinoptilolite.

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#### ГЕТЕРОПОЛИҚЫШҚЫЛДАР НЕГІЗІНДЕГІ КРЕКИНГ КАТАЛИЗАТОРЫ

**Аннотация.** Гетерополиқышқылдар (ГПК) күшті брэнстедті қышқылдар болып табылады. ГПК 12 катардағының катализ үшін маңызы өте зор. Жұмыстың мақсаты – Шанханай кен орыны табиғи цеолиті

негізінде крекинг катализаторының құрамын жасау. Катализаторды модифицирлеу минералды, органикалық қышқылдармен және ГПК жргізілді. Дайындалған катализатор физикалық-химиялық әдістермен зерттелді. ИК-спектроскопия нәтижелеріне сәйкес табиғи цеолит декатионирлеу мен деалюминирлеуден кейін өзінің кристалдық құрылымын өзгертпейді. Модифицирлеу кезінде ГПК мен цеолит арасында байланыс түзілетіні болжанды. Электронды микроскопия мәліметі бойынша  $PW_{12}$ -ГПК бөлшектері клиноптилолит бетінде жоғары дисперстілік дәрежесінде таралады. Цеолит бетін ПЭМ ВР әдісімен зерттегенде өлшемі 1-2 нм тұрақты кластерлі құрылымның түзілгенін көрсетті. Бұл кластерлер цеолит бетінде тепе-теңдікте таралған және әрекеттесуші заттарға қолайлы.

**Тірек сөздер:** катализдік крекинг, гетерополикышқылдар, Шанханай кенорынының цеолиті, электронды микроскоп.

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#### **КАТАЛИЗАТОРЫ КРЕКИНГА НА ОСНОВЕ ГЕТЕРОПОЛИКИСЛОТ**

**Аннотация.** Гетерополикислоты (ГПК) являются сильными бренстедовскими кислотами. ГПК 12 ряда имеют наибольшее значение для катализа. Цель работы – разработка состава катализаторов крекинга на основе природного цеолита Шанканайского месторождения (Казахстан). Модифицирование катализаторов проводилось минеральными кислотами, органическими кислотами и ГПК. Катализаторы всесторонне исследованы комплексом физико-химических методов. По данным ИК-спектроскопии после декатионирования и деалюминирования природный цеолит не изменяет свою кристаллическую структуру. Предположительно, происходит образование связи ГПК с цеолитом при модифицировании цеолита ГПК. Данные электронной микроскопии говорят о высоких степенях дисперсности и распределения частиц  $PW_{12}$ -ГПК по поверхности клиноптилолита. Детальное изучение поверхности цеолита методом ПЭМ ВР показало образование устойчивых структур кластеров размером 1-2 нм, которые частично внедрены в объем цеолита. Эти кластеры равномерно распределены по поверхности цеолита и доступны для реагирующих веществ.

**Ключевые слова:** каталитический крекинг, гетерополикислоты, цеолит Шанканайского месторождения, электронная микроскопия.