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SH. N. ATAULLAYEV, B. A. MAVLANOV, S. F. FOZILOV,
V. N. AKHMEDOV, A. U. OCHILOV, M. M. TILAVOVA*

Bukhara engineering-technological institute, Bukhara

PHYSICAL-CHEMICAL PROPERTIES OF CATALYSTS FOR DESTRUCTIVE HYDROGENIZATION OF OIL DEASPHALTIZATE

Abstract. The physicochemical and catalytic properties of catalysts and their preparation for destructive hydrogenation of asphalt-free oil are found out in the article. Favorable conditions for obtaining effective catalysts of the hydrogenation process were determined. Also, the process of thermal regeneration of the working zeolite and the surface-acid properties of the Ca-zeolite catalyst was studied.

Key words: catalyst, deasphaltizate, destruction, hydrogenization, thermo-regeneration, adsorbent, zeolite, regeneration, sieve, extrudate.

Introduction. It is known that catalysts containing metals of Group VIII of Mendeleev's (Pt, Pd, Co, Ni and etc.) periodic system possess high hydrogenating properties. But their use for hydroprocessing petroleum products with sulfur-, nitrogen-, oxygen- and organometallic impurities is inexpedient, since they are rapidly poisoned. In the hydro processing of residual petroleum products, the depth of their conversion, the quality and quantity of the "light" distillates thus formed depends on the catalytic properties of the using catalysts [1, 2].

It is established that the use of nickel in combination with molybdenum makes it possible to obtain a catalytic system with hydrodehydrogenic and acidic properties, and when this system is converted into a sulphide form, the activity, the functionality of the system in acid catalysis is more increased. Nickel is a molybdenum system because it is the most active catalyst of processes: for hydrogenation, isomerization, dehydrocyclization, hydrodenitrogenation, hydrodesulfuration, it exhibits polyfunctional properties, is stable to the deactivating actions of sulfur-, nitrogen-, oxygen-organic compounds. Treatment of this system with a sulfur organic compound or hydrogen sulphide increases its activity in redox and acid catalysis. In view of the above, the elaboration of polyfunctional catalysts for the destructive hydrogenation of oil deasphaltizate was carried out on the basis of nickel and molybdenum compounds on various refractory acid supports: spent zeolite after thermal regeneration $ZnAl_2O_4$ and $BaAl_2O_4$ [3-6].

Due to their specific surface properties, crystalline aluminosilicates are widely used as a carrier and isomerizing phase in multicomponent catalysts. Depending on the type and concentration of acid sites of zeolites, especially CaA, they are widely used in isomerization, alkylation, polymerization, cracking, hydrocracking processes.

Synthetic zeolites are widely used in various industries. The large-tonnage consumer of zeolite CaA as an adsorbent is the Shurtan gas processing plant. Due to the lack of a local zeolite, it is purchased for foreign currency. At present, a huge amount of environmentally hazardous industrial waste is accumulated in the dumps of the plant - the spent adsorbent CaA, which is subject to regeneration, which can be used for the production of local zeolite. Taking this into account, using modern physicochemical methods of analysis that allow us to study the processes occurring during the processing of the spent zeolite, we have established methods for regenerating the adsorbent in which the zeolite retains its structure and exhibits high surface acidic properties, which makes it possible to use it as a destructive hydrogenation catalyst oildeasphaltizate.

RESULTS AND DISCUSSION

Investigation of the process, thermal recovery of spent zeolite. It is known that the thermal treatment of zeolites allows the removal of impurities, especially of organic nature. The thermograms of spent CaA zeolite obtained from the Shurtan MCC are given in figure 1. As follows from the thermogram, the exoeffect at 200 °C corresponds to the removal of structural water. The pronounced exothermic effect with a maximum at 362 °C refers to the removal of the residual part of organic compounds adsorbed in the purification of natural gas containing sulfur, nitrogen and resinous substances. Weak "Exoeffects" in the region of 500-600 °C are due to the burnout of strongly adsorbed organic substances, which is accompanied by a slight weight loss, and from 700 to 990 °C, zeolite is sintered without losing weight.

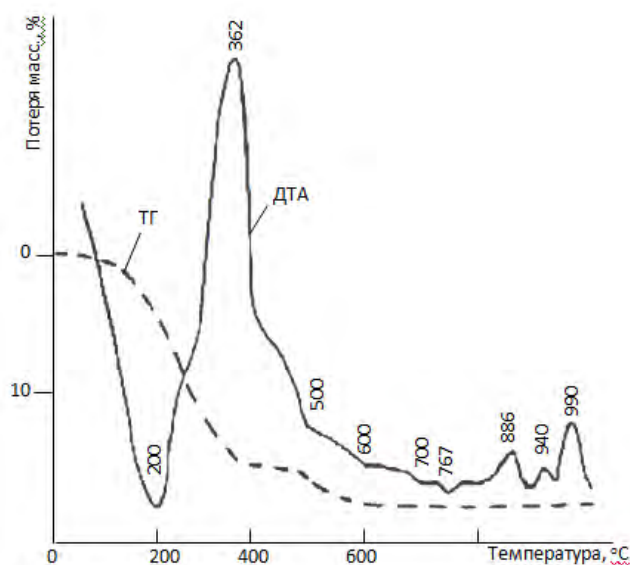


Figure 1 – The thermogram of spent CaA zeolite, obtained from Shurtan MCC

Thus, the temperature ranges for the recovery of the spent CaA zeolite and the limits of the temperature effect on this sorbent were established, and its surface-acid properties were investigated.

In practice, in order to increase the surface acid properties of the zeolite, it is activated by anions of mineral acids. In our case, the thermoregenerated zeolite is activated by an aqueous solution of acids HCl, H₂SO₄ and HNO₃. The activation carried out for 11-12 hours at room temperature. Table 1 shows the results of the study of the change in the surface acid-base properties of the zeolite calcined at 600 °C, depending on the concentration of acid.

Sounding of acid sites by the position of the absorption peak of the indicators was carried out: a) after adsorption on samples without preliminary heat treatment; b) after drying at 200 °C; c) after calcination at 600 °C. The results of the study showed that on hydrated samples phenolphthalein is adsorbed in a colorless acid form, i.e. the main centers with $pK_a \geq 9,3$ are absent. Bromphenolblau - an indicator for weakly acid centers with $pK_a \approx 3,8$ is adsorbed on hydrated samples mainly in two forms. As a result of adsorption on weakly acid and weakly basic centers, ($3,8 < pK_a < 9$), an absorption band with high extinction is observed in electronic spectra, the maximum of which is about 600-610 nm (the first form), the presence of centers with $pK_a < 3,8$ indicates the appearance of a less intense absorption band at 430 nm (the second form) from bromophenolblau ionized at acid sites. On samples activated with 5% hydrochloric acid, only acid sites with pK_a of less than 3.8 are observed. A similar picture is observed for the indicator benzazolazodiphenilamin $pK_a \leq 1,5$. A study of the surface of the samples dried at 200 °C before the beginning revealed the presence of Brønsted type centers with pK_a about -3. Only the samples treated with 3.0% sulfuric and nitric, as well as 5.0% hydrochloric acid, found stronger Brønsted centers with $pK_a \leq -6$.

The strength and concentration of acid sites is increased by an increase in the pretreatment temperature of the surface to 500 °C. Moreover, in addition to proton ones, Lewis acid sites are also identified on individual samples (table), which disappear at dehydration. It is known that, under equal conditions, the acidity of various types of zeolites increases with an increase in the degree of exchange of metal ions with protons. In the absence of information on the degree of exchange of aluminum and calcium ions, we have attempted to find a correlation between the concentration of acid sites and the concentration of the activating solution containing these ions. From the data of table 1 it can be noted that within each series of samples the maximum concentration of strong acid sites is $-6 < pK_a < -3$, for samples calcined at 600 °C just before probing and $-6 < pK_a < -3$ for samples dried at 200 °C, for activation with a 5.0% solution of hydrochloric acid. At the same time, the concentration of the centers on the samples prepared at 600 °C increases markedly. It is here that aprotic acidic centers are observed, which are particularly pronounced in the case of treatment of sulfuric acid zeolite. As follows from the data in table 1, activation of thermoregenerated zeolite with an aqueous solution of mineral acids enhances its surface-acid properties to a certain

The change of surface of the zeolite calcined at 600 °C depending on the concentration acid and its acid-base properties

Samples and condition	Concentration (mmol/g) of acid-base centers with pKa on the surface of activated solutions and mineral acids with different concentrations							Site type
	-8	-6,3	-5,6	-3,3	+1,5	+3,8	+9,3	
1. Spent (unregenerated)	-	-	-	0,05	0,13	0,38	-	B + L
2. Thermoregenerated (without activation)	-	0,08	0,09	0,24	0,34	0,47	-	B + L
3. Activated by acid at 20-25°C, during 11-12 hour	-	0,20	0,21	0,22	0,32	0,40	-	B
0,1% HCl	0,04	6,07	0,12	0,18	0,27	0,32	-	B
4. 1,0% HCl	0,03	0,24	0,24	0,32	0,37	0,39	-	B
5. 2,5% HCl	-	-	0,03	0,08	0,30	0,30	-	B
6. 5,0% HCl	-	0,8	0,20	0,20	0,21	0,30	-	B
7. 3,0% HNO ₃	-	0,04	0,07	0,13	0,15	0,21	-	B + L
8. 3,0% H ₂ SO ₄	-	-	-	-	-	-	-	-

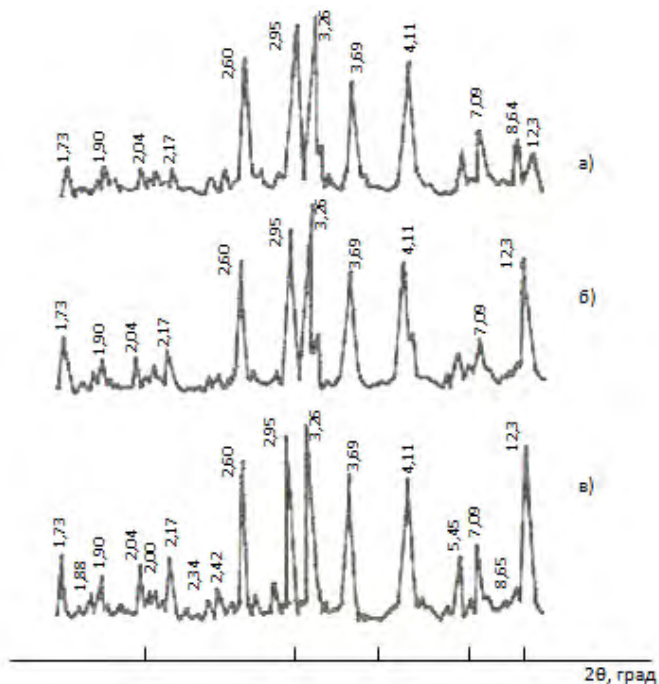


Figure 2 – X-ray patterns:
 a) initial zeolite; b) a thermoregenerated zeolite;
 c) a zeolite activated with hydrochloric acid

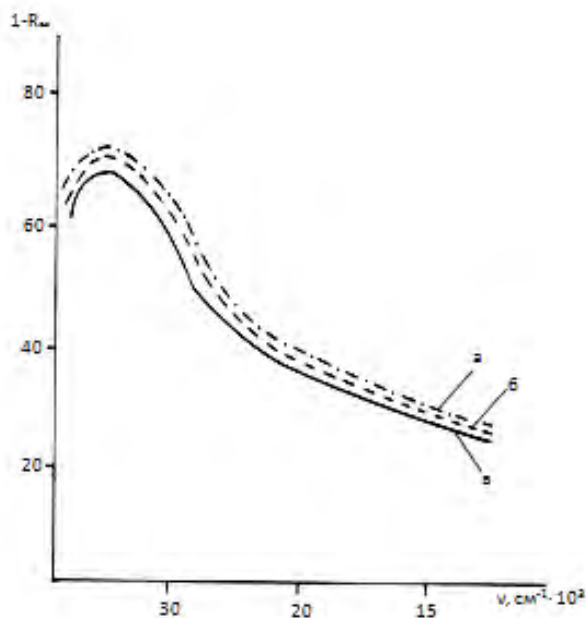


Figure 3 – ESD of zeolite CaA: a) thermoregenerated;
b) activated by 1.0; 2.5; 5% HCl solution and dried at 200 °C; c) calcined at 600 °C

extent, which increase with an increase in the concentration of the activating acid to 2.5%, and then decrease. The activating action of solutions of sulfuric and nitric acid is much lower than that of hydrochloric acid. Taking into account that the isomerization reactions proceed mainly on acidic centers with $pK_a = -3,3 \div 3,8$ mmol/g, an aqueous solution of hydrochloric acid with a concentration of 0,1% was used as an activating additive. In the process of processing the thermoregenerated zeolite with this solution, a whole set of acid sites of various strength and concentration appears on the surface of the adsorbent. In the regenerated zeolite, its structure does not change, as evidenced by the X-ray diffraction pattern (figure 2, a, b, c) and ESTD (figure 3, a, b, c).

Conclusion. Thus, when studying the process of thermoregeneration of spent zeolite, the temperature ranges for the recovery of spent CaA zeolite and the limits of the temperature effect on this sorbent were established, the effect of mineral acid anions on the surface-acid properties of CaA zeolite was studied. Based on the data obtained, methods for the preparation of catalysts for the destructive hydrogenation of oildeasphaltizate have been developed and their physicochemical and catalytic properties have been studied.

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Резюме

*Ш. Н. Атауллаев, Б. А. Мавланов, С. Ф. Фозилов,
В. Н. Ахмедов, А. У. Очилов, М. М. Тилавова*

МУНАЙ ДЕАСФАЛЬТИЗАТЫН ГИДРОГЕНИЗАЦИЯЛАУҒА АРНАЛҒАН КАТАЛИЗАТОРЛАРДЫҢ ФИЗИКО-ХИМИЯЛЫҚ ҚАСИЕТТЕРІ

Мұнай деасфальтизатын гидрогенизациялауға арналған катализаторларды алу және олардың физико-химиялық қасиеттері зерттелген. СаА-түріндегі цеолитті қайтақ қалпына келтіру үшін терморегенерациялау және цеолит бетіндегі қышқылдық орталықтар қарастырылған.

Түйін сөздер: катализатор, деасфальтизат, деструкция, гидрогенизациялау, терморегенерациялау, адсорбент, цеолит, қыздыру.

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*Ш. Н. Атауллаев, Б. А. Мавланов, С. Ф. Фозилов,
В. Н. Ахмедов, А. У. Очилов, М. М. Тилавова*

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА КАТАЛИЗАТОРОВ ДЛЯ ГИДРОГЕНИЗАЦИИ ДЕАСФАЛЬТИЗАТА НЕФТИ

В работе приведены способы получения катализаторов для деструктивной гидрогенизации деасфальтизата нефти и изучены их физико-химические и каталитические свойства. Также исследованы процесс терморегенерации отработанного цеолита и поверхностно-кислотные свойства катализаторов на основе цеолита СаА

Ключевые слова: катализатор, деасфальтизат, деструкция, гидрогенизация, терморегенерация, адсорбент, цеолит, прокалка.