DEVELOPMENT OF TECHNOLOGIES FOR PRODUCING CATALYST FOR DESTRUCTIVE HYDROGENIZATION OF ASPHALT-FREE OIL OF HEAVY SULFUR OIL

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INTRODUCTION

In the main directions of development of Uzbekistan, special attention is paid to the energy complex, where priority is given to the oil refining industry [1]. Unfortunately, the lack of own competitive catalysts and flexible technologies for hydrogenation processes makes it impossible to more efficiently process heavy, high-paraffin, sulfurous and resinous local oils [2,3]. Therefore, in recent years, the requirements for the environmental safety of the production and improvement of the running ability of commercial petroleum products, natural and process gases have risen sharply against the background of a high content of paraffinic, aromatic and sulfur compounds in the processed crude oil.

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 hydro processing petroleum products with sulfur-, nitrogen-, oxygen- and organometallic impurities is inadmissible, 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. It is established that the use of nickel in combination with molybdenum makes it possible to obtain a catalytic system with hydrodehydrogenising and acidic properties, and when this system is converted into a supplied 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, hydronitrogenation, 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 supplied increases its activity in red ox and acid catalysis. In view of the above, the elaboration of polyfunctional catalysts for the destructive hydrogenation of oil deasphaltize was carried out on the basis of nickel and molybdenum compounds on various refractory acid supports: spent zeolite after thermal regeneration ZnAl2O4 and BaAl2O4 [4-6].

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 oldeasphaltize.

METHODOLOGY AND DATA

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. 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 ° C to 990 ° C, zeolite is sintered without losing weight.

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 thermo regenerated zeolite is activated by an aqueous solution of acids HCl, H2SO4, HNO3. The activation was 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 the activating acid.

**Table 1. The change in the surface acid-base properties of the zeolite calcined at 600 °C, depending on the concentration of the activating acid.**

| Experimental samples | Concentration (mmol/g) of acid-base centers with pKa on the surface of activated solutions and mineral acids with different concentrations | Sitetype |
|----------------------|---------------------------------------------------------------------------------------------------------------------------------|----------|
|                      | -8                                                                                                                             | -6,3     | -5,6 | -3,3 | +1,5 | +3,8 | +9,3 |       |
| 1. Spent (unregenerate) | -                                                                                                                             | -        | 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 (0,1% HCl at 20-25°C, τ = 11-12 hour) | -                                                                                                                             | 0,20     | 0,21 | 0,22 | 0,32 | 0,40  | -     | B     |
| 4. Activated 1,0% HCl | 0,04                                                                                                                           | 6,07     | 0,12 | 0,18 | 0,27 | 0,32  | -     | B     |
| 5. Activated 2,5% HCl | 0,03                                                                                                                           | 0,24     | 0,24 | 0,32 | 0,37 | 0,39  | -     | B     |
| 6. Activated 5,0% HCl | -                                                                                                                             | -        | 0,03 | 0,08 | 0,30 | 0,30  | -     | B     |
| 7. Activated 3,0% HNO3 | -                                                                                                                             | -        | 0,20 | 0,20 | 0,21 | 0,30  | -     | B     |
| 8. Activated 3,0% H2SO4 | -                                                                                                                             | 0,04     | 0,07 | 0,13 | 0,15 | 0,21  | -     | B + L |

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 1), 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.
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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 paretic 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 the thermoregenerated zeolite with an aqueous solution of mineral acids enhances its surface-acid properties to a certain 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 $pK_a = -3.3+3.8$ 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 (Fig. 2, a, b, c) and ESTD (Fig. 3. a, b, c). 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 oildesphalizate have been developed and their physicochemical and catalytic properties have been studied [7,8].

Hydrogenation processes are necessary to increase the yield and improve the running abilities and environmental qualities of the received petroleum products. At the same time, the efficiency of the hydroprocess largely depends on the catalytic properties of the used catalyst, mainly on its hydrogenating properties and their stability to the deactivating effects of heteroatomic organic compounds present as impurities in the feedstock. Due to the fact that during the hydrogenation processing of petroleum products of various origin, the conversion of undesirable hydrocarbon and non-hydrocarbon components into effective hydrocarbons proceeds through the hydrogenation stage, it becomes necessary to use hydrogenating catalysts to accelerate the reaction. Therefore, the higher the hydrogenating activity of the catalyst,
the more the yield of the resulting oil products increases and their quality improves.

Proceeding from this, we, on the basis of local raw materials, developed catalysts for the directed processes of destructive hydrogenation of the asphalt-free oil of heavy sulfur oils.

The technology of preparation of the catalyst based on a compound containing nickel-molybdenum on thermally generated CaA zeolite was carried out in the following way.

The basic technological scheme for the preparation of a catalyst containing zeolite-nickel-molybdenum using the used CaA adsorbent is shown in Fig. 4.

This technological scheme consists of the following successive after other processes:

- thermal regeneration of zeolite;
- deposition of a nickel compound on it;
- deposition of molybdenum on nickel containing zeolite;
- calcination of nickel-molybdenum-containing zeolite;
- packaging and shipping of finished nickel-molybdenum catalyst.

Thermal regeneration of spent CaA (DGT-11) type zeolite is carried out in a tempering unit 2', 2'', 2''' at 580-600 °C and a weak current of atmospheric air for 5.5-6.0 hours. After the end of this procedure, the temperature in the furnace is reduced. Then, in order to release the regenerated extradite from dust, chips, and products formed during burnout of adsorbed organic substances, it is first sieved through a sieve 9 with openings of 0.8-1.0 mm cells. Then rinse with clean dry air with a temperature of 50-60 °C. Then, in the impregnating device 3', 3'', on the zeolite CaA, using a spray gun 4', 4'', in the form of an water solution, the nickel compound is applied by uniform mixing.

The finished molybdenum-nickel-zeolite-containing catalyst is packaged in plastic bags, placed in 200-liter barrels with a hinged lid and shipped to consumers.

Thus, according to the above described technology, the prepared catalyst is used for the process of destructive hydrogenation of asphalt-free oil.

Preparation of polyfunctional catalyst DHT - 13. The basic technological scheme of production of the nickel-molybdenum system is shown in Fig. 5. Into the mixer (pos. 5) equipped with a heated system and an agitator, from the measuring device (pos. 1) 4 l of distilled water is poured, and then 3.399 kg of ammonium molybdate salt [(NH₄)₆Mo₇O₂₄·4H₂O, ГОСТ 3765-78, “chda”), are introduced with stirring, which gradually with uniform stirring and heating is brought to complete dissolution and the formation of a true solution. Then, while continuing to mix the molybdenum salt solution while heating until the formation of a pasty mass, 4.156 kg of the nickel nitrate salt [(Ni(NO₃)₆]·6H₂O, ГОСТ 4055-78, “chda”), are gradually introduced, the resulting mass is transferred to the trays (pos. 14) and subjected to heat treatment (pos. 7). The tempering of the nickel-molybdenum complex is carried out in the temperature range at which the complete decomposition of nickel and molybdenum salts to the corresponding oxides and their interaction with the

![Figure 4. Schematic diagram of the production of the catalyst DGT-11.](image)
formation of nickel compounds with molybdenum. After the end of the heat treatment of the mixture, the temperature of the furnace is reduced to room temperature; the resulting nickel-molybdenum system is discharged from the furnace, and is used as an active hydrodehydrating component for the polyfunctional catalyst DHT-13.

Preparation of acid carrier - zinc acuminate. 5.48 kg of precipitated aluminum oxide hydrate with 36.2% moisture and 28 kg of zinc oxide powder are loaded into the mixer, similar in construction to the mixer for preparing hydrodehydrating catalyst components (pos.1); the mixture is homogenized for 12-15 minutes, then with stirring, 3.6 l of distilled water is introduced into it and continue to homogenize for 35-40 minutes (in the case, to obtain a homogeneous, uniform doughy mass in order to avoid lumpy and difficult to mix, it is allowed to entry additional amount of water). Then the mass is transferred to 4-5 cm thick trays (pos.14) from stainless steel and sludge it in the open air for 10-12 hours, then the mass is transferred to the electric stove furnace (pos. 6), where it is heat treated at 550-560 ° C for 4.5-5.0 hours, at which the complete interaction of Al(OH)₃ nH₂O with ZnOoccurs with the formation of zinc acuminate [ZnAl₂O₄].

The basic technological scheme of the production of catalyst DGT-13

1, 2, 11- measuring tanks; 3- solvent; 4, 5, 12- mixers; 6, 7, 15-puncture aggregates; 8- scales; 9- adsorber-neutralizer; 10-ball mill; 13- molding machine; 14 - racks; 16 - sieve; 17- barrels for the finished catalyst. I- tank for air cleared of NOand NH₃; II- tank for 10-12% NaOH solution; III- to the ball mill

After the end of the heat treatment, the furnace temperature is reduced by 50-60 ° C per hour to room temperature; the zinc acumin thus obtained is used as an acid carrier of the active hydro dehydrating catalyst components.

RESULTS
Nickel molybdate application on zinc acuminate. To 2.4 kg (in terms of 100% ZnAl₂O₄) zinc aluminate 0.6 kg (in terms of 100% dry product) active mixture the consisting of nickel oxides and molybdenum in the form of nickel molybdates injected. The resulting mixture is loaded into a ball mill (10), muffle loading-unloading hatch, starting the electric motor grind it for 40-45 minutes to a powder-like state. After the end of grinding turn off the electric motor, replace the manhole plugs with a sieve of 2.0-2.5 mm in cell size and turn on the electric motor. The crushed mass is sieved, the mixture is collected in the drums, then sent to the mixer to transfer the mixture into the paste [9,10].

The receiver powder of catalyst system is weighed on a commodity scale (pos. 8), loaded into a mixer (pos. 12) equipped with a Z-shaped stirrer, where, with stirring, 0.45-0.5 kg (16 % of the mass of the powder) B-311 add from measuring tank to bind the mixture and stirred for 30-35 minutes until a homogeneous plastic mass is formed. The catalyst mass in the form of dough thus obtained is first discharged into trays, from there - into the bunker of the molding unit - an extruder, which for PPC catalyst masses going to the molding in the screw machine is set to 16-17%.

The molded extricates take on trays with a thickness of 13-15 mm, which are replaced with empty ones as they fill, the filled trays in the racks are sent again to the wilting. Dry-cured in the open air for 10-12 hours, the extrudates are sent to the chamber of the tempering furnace. The tempering of catalyst is carried out at a temperature of 500-550 ° C for 16-24 hours. After the end of the heat treatment of the catalyst, the furnace is turned off and observing the temperature reduction mode at 25-30 ° C per hour, reducing it to room temperature, then unloading the catalyst into the barrels, packing and send them to the destination.

Thus, the resulting catalyst can be used for the process of destructive hydrogenation of the asphalt free oil obtained from crude oil.

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