ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

2 (62)

АПРЕЛЬ – ИЮНЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

УДК 665.656.2

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INVESTIGATION OF THE PROCESS OF APPLICATION OF SALTS OF ACTIVE PHASES OF NICKEL AND MOLYBDEN TO THERMOREGENERATED ZEOLITE CaA

Abstract. In this work, studies are carried out the process of applying active phases of nickel and molybdenum compounds to thermoregenerated CaA zeolite and heat treatment of catalytic systems based on it.

Key words: catalyst, thermoregeneration, adsorbent, zeolite, regeneration, application, mixing, activated, thermal analysis, calcinations, chemisorption, endothermic and exothermic effect.

Introduction. It is known that the depth of hydroconversion of the components of the feedstock, the quality and quantity of the target oil depends on the hydrogenating and isomerizing properties of the catalyst used: the more active the contact in these reactions, the deeper the hydroconversion of the raw materials in the low boiling distillates, the higher the quality and the greater the yield of the desired product. The catalysts containing noble metals (Pt, Pd, etc.) possess high hydrogenating and isomerizing properties.But because they have low hydrogenating and isomerizing activity, they are unacceptable for hydroprocessing residual petroleum products containing contact poisons, and the desired results can not be obtained on industrial Al-Ni (Co)-Mo catalysts. At the same time, the catalyst containing a nickel on hydrogenating activity can compete with catalysts based on platinum and palladium, but it is also committed to poisoning with sulfur and nitrogen containing compounds. The use of nickel in combination with molybdenum in the form of nickel molybdate allows the preparation of a catalyst having simultaneously high hydrogenating, isomerizing and cleaving properties. Treatment of the catalyst with sulfur or hydrogen sulphide increases its polyfunctionality in acid catalysis [1, 2].

It has been established that nickel - molybdenum catalysts on various refractory acid carriers exhibit higher activity and stability in oxidation - reduction and acid - base catalysis in the case of exclusion or reduction of the formation of catalytically inactive nickel aluminate by spinel structure.

EXPERIMENTAL PART

To study the processes occurring at the stage of applying active phases to the thermo regenerated and regenerated zeolite and heat treatment of catalytic systems, the following samples were prepared:

Sample 1 (CM). It is prepared by applying the calculated amount of molybdenum salt in the form of an aqueous solution to the thermo regenerated and activated zeolite CaA. After drying in the open air, the sample was subjected to thermal analysis.

Sample 2 (CMN). The air-dry catalyst was obtained by applying the calculated amount of nickel salt in the form of an aqueous solution to a CM sample pre-calcined at 550 °C.

Sample 3 (CN). It is prepared by applying an aqueous solution of a nickel salt to a thermoregenerated zeolite, then the order of the sequence and sequence are the same as for the treatment of a CM sample.

Sample 4 (CNM). It is prepared by calcination of the sample of the CN at 550 °C, followed by applying the calculated amount of the molybdenum salt in the form of an aqueous solution. An air-dry system was subjected to thermal analysis.

RESULTS AND DISCUSSION

On the thermogram of the spent zeolite, an "endothermic" effect at 200 °C with an inflection point at 280 °C, corresponding to the removal of physically adsorbed water is clearly visible. And the stepwise removal of chemisorbed water, localized in various cavities, for CaA type zeolites proceeds most intensively, in the range from 350 to 450 °C. In addition, an "exothermic" effect was observed, due to the removal of organic deposits from the pores of zeolite CaA.

The thermogram of the spent zeolite shows that the intense exothermic effect at 360 °C, from the burnout of organic compounds, overlaps the weaker endothermic effects from the dehydration of the zeolite. The presence of these effects indicates the preservation of the specific crystal structure of the zeolite and its ability to reverse water adsorption. The preservation of crystalline structures was proved by the RFA diffraction method, X-ray diffraction and the weighting method for "adsorption-desorption" of water. The effects on the thermograms of catalyst samples with supported transition metal ions were found to be related.The following effects were observed on the thermogram (figure 1b) of crystalline nickel nitrate: a narrow peak at 65 °C, two more intense broad peaks at 190 and 320 °C, and a small "endoeffect" is observed at 255 °C.

On the thermogram of nickel nitrate deposited on a thermoregenerated zeolite (figure 2b of a sample of CNM) and dried at 20-25 °C, τ = 24-26 hours, a very wide low-intensity endoeffect with a maximum at 150 °C is observed, accompanied by a slight loss of mass on the curve TG, due to the removal of residues of physically adsorbed water. There is no specific narrow endoeffect from the thermal decomposition of crystalline nickel nitrate, the position of higher temperature peaks also does not correspond to the initial substance, all this indicates the occurrence of deep chemical transformations already at the stage of impregnation. Taking into account the strongly alkaline environment during the application of nickel nitrate due to the release of compensating calcium ions into

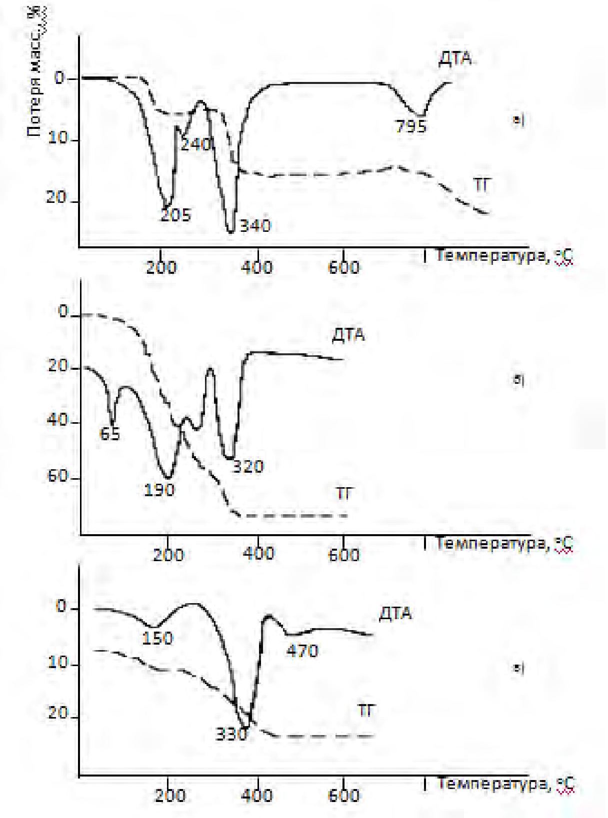

Figure 1 – Thermogram of nickel and molybdenum compounds:
a) ammonium para-molybdate; b) nickel nitrate; c) nickel hydroxide

the solution, it is possible to assume the formation of the Ni (OH) $_2$ hydrogel, which is characterized by two little intense broad peaks of the endoeffect at 150 and 470 °C, in addition to the powerful endo-effect, temperature 330 °C, the main weight loss of the sample is observed (figure 1c).

Comparison of the thermogram of the CMN sample with the thermograms $Ni(OH)_2$ and $Ni (NO_3)_2 \cdot 6H_2O$ allows us to consider this DTA as a superposition of the stepwise thermal decomposition of the most probable products of basic hydrolysis, namely, hydroxy complexes of nickel nitrate, its basic salts and hydroxides. Apparently, DTA of the investigated sample of CMN is closest to DTA $Ni(OH)_2$, where there are strongly broadened effects at 150 and 290-330 °C, and "endoeffects" at 400 and 620 °C are most likely due to removal of intracrystalline zeolite water.In the case of thermal decomposition of nickel nitrate deposited on an acid-activated zeolite (figure 2a and a sample of a CN), the thermal effects from the dehydration and thermal fixing of nickel structures on the zeolite are shifted to the low-temperature region.

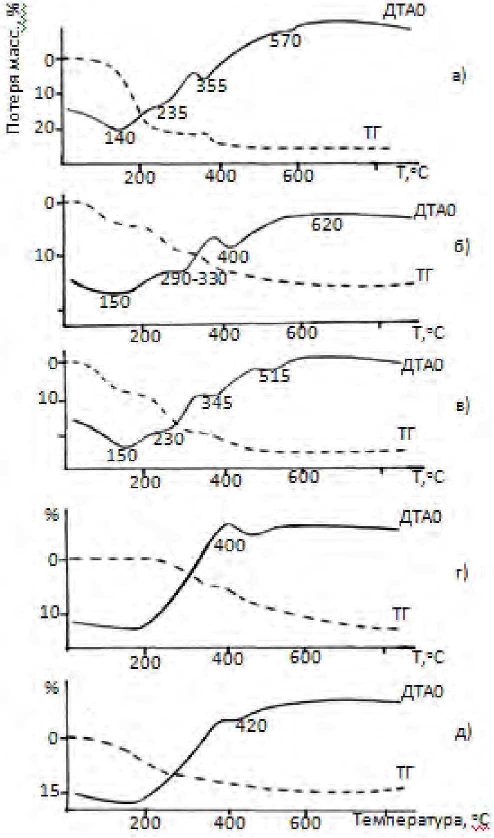

Figure 2 – Thermogram of zeolite catalysts:
a) a sample of the CN, b) a sample of CNM, c) a sample of CMN, d) a sample of CM

This may indicate, according to the ESTD, the prevalence of nickel hydroxo-complexes over nickel hydroxide in a dried but not calcined sample; avariety of nickel structures are observed in the calcined sample.The reaction products of hydrolyzed nickel nitrate with molybdenum compounds thermally fixed on the surface of the activated zeolite dehydrate at lower temperatures than in the case of an activated and the more thermoregenerated sample and may be associated with the dehydration of nickel-molybdate associates. The "exothermic" effect (figure 2, model CM) can be noted on the DTA curve of the CM sample (see figure 2, which is accompanied by a weight loss), which can be explained by the thermal decomposition of the ammonium form of the zeolite formed as a result of ion exchange of the compensating calcium ions with ammonium ions during the impregnation of the zeolite solution of ammonium para-molybdate. On the DTA curve of ammonium para-molybdate, according to (figure 1a), "exoeffect" is not observed, only "endoeffects" at 205, 240, 340 and 795 °C were noted.In our case, the "exothermic" effect of the transition of the ammonium form of the zeolite to hydrogen does not appear to be due to the fact that during the preliminary application of nickel nitrate followed by calcination (figure 2a), the nickel cations are firmly fixed in the zeolite cavities, and the ion-exchange of Ca^{2+} on NH_4^{+} does not occur. The absence of "endoeffects", specific for the thermal decomposition of ammonium para-molybdate, indicates a deep chemical interaction already during impregnation. Smooth weight loss in the temperature range 100-500 °C without pronounced thermal effects is due to the gradual removal of water. Ammonium ions are displaced from ammonium para-molybdate by a stronger base - calcium hydroxide and removed to the drying process of the sample. Due to the fact that the thermal decomposition of the formed calcium molybdate occurs at a temperature of 1000-1100 °C, it does not appear in the investigated range on the DTA curve.

Electronic diffusion reflection spectra (EDS) of molybdenum - nickel and nickel - molybdenum catalysts on a thermoregenerated zeolite are shown in figure 3 and 4.

Spectra of catalysts were taken in the 50-5cm-1 region on a Hitachi-330 spectrophotometer with a diffusion reflection attachment. It follows from figure 3 and 4 when applying an aqueous solution of nickel and molybdenum salts to CaA zeolite, complex processes occur on its surface that promote the formation of various compounds: $CaMoO_4$, $NiMoO_4$, and other oxygen compounds of nickel and molybdenum. Calcium molybdate clearly appears in the roentgenograms of the calcined catalyst and can overlap the baseline with d = 3.08Å from the crystalline nickel molybdate. However, the absence of narrow lines with d = 2.73 and 2.06 Å on X-ray diffraction patterns indicates a high dispersion of the nickel-molybdate structures formed. Nickel-molybdate associates appear as broad bands from Ni^{2+} with maxima at 12.9; 20.0; 23.2; 26.6 cm^{-1}. The highly dispersed phase

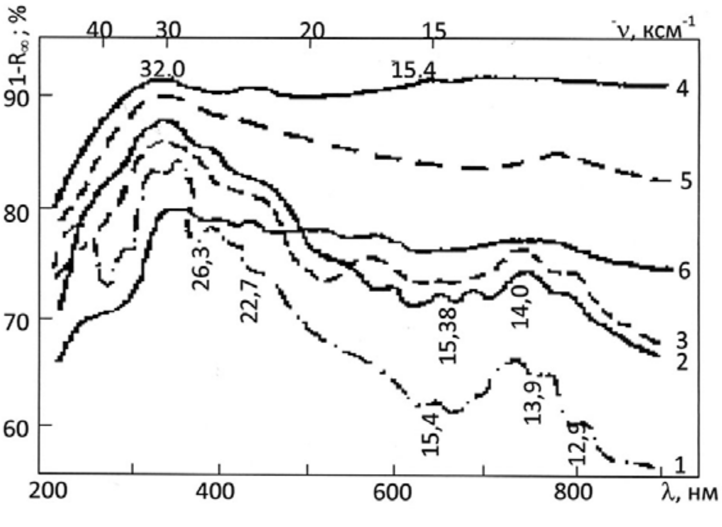

Figure 3 – Electronic spectra of diffuse reflection of nickel-molybdenum catalyst, reduced at 300 °C - (1), 320 °C - (2,3), 360 °C - (4-6) and reoxidized at 25 °C - (3,5) and 360 °C - (6)

of nickel oxide was identified by the pronounced band 13.9 cm^{-1} and a number of diffuse bands at 15.4; 21.8; 23.2; 25.0 cm^{-1}. In a large region at 26.3 and 27.7 ks^{-1}, Mo^{5+} ions are also absorbed, whose presence is confirmed by the decrease of these bands after oxidation of the latter with hydrogen peroxide to Mo^{6+}. Mo^{6+} ions appear in the spectra with a broad absorption band with a maximum of 29.4 ± 30.7 ks^{-1} and a shoulder of about 41.7 ks^{-1}. ts high intensity and some shift to the low-frequency region indicate the predominance of structures of the Mo^{6+}_{Td} - O - Mo^{6+}_{oh} type, which determine the presence of Brönsted acid sites with pKa<-3 on the surface of the catalyst.

The ESD of the nickel-molybdenum catalyst on the thermoregenerated zeolite is given in figure 4. It follows from the picture that in the catalyst, as in the previous one, $CaMoO_4$, $NiMoO_4$ and other compounds are present. But, the intensity and quantity of $CaMoO_4$ formed is lower than when nickel is applied to calcined molybdenum-zeolite.

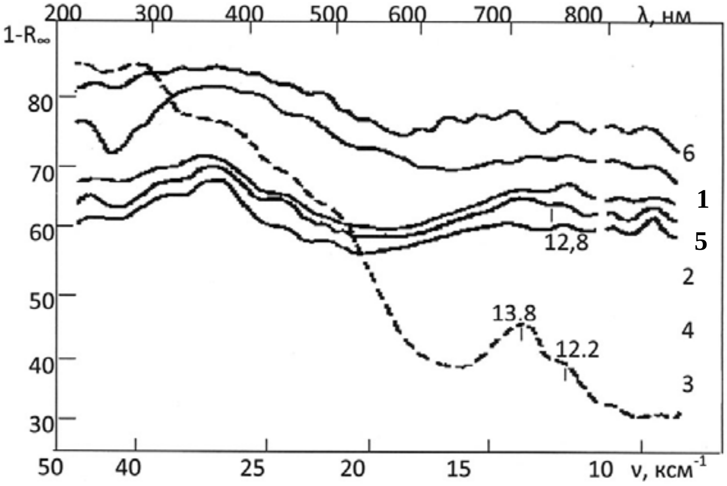

Figure 4 – EDS of catalysts on a thermoregenerated (1-2) and activated by 0.1% HCl zeolite (3-6). Air-dry (1.3), calcined 823 K (2,4-6). The ratio of NiO: MoO_3 = 1: 1 - (1-4)

The appearance of new absorption bands in the spectrum of about 12,8 and 12,8 ksm^{-1} is associated with the formation of fragments of nickel-molybdate structures in dried samples when ammonium para-molybdate is applied to calcined nickel-zeolite systems. After calcination, the spectrum consists of an extended absorption band with a maximum of 12.9 ksm^{-1}, moderate bands at 20,0; 23,8 ksm-11 and an intense wide band of Mo^{6+} ions occupying the entire UV region, which is typical for molybdate-nickel. That is, acid activation and pre-fixing of nickel structures on the zeolite contribute to the formation of nickel-molybdenum associates. To study the x-ray composition of the nickel-molybdenum catalyst on the thermoregenerated and activated zeolite, the following samples were prepared with the ratio NiO: MoO_3 1: 1 (No. 1), 1: 2 (No. 2) and 2: 1

(No. 3). X-ray patterns of the samples are shown in figure. 5. It can be seen from the figure that almost all lines characteristic of CaA zeolite are present in all the samples. Thus, in sample No. 1, CaA exhibits an average degree of crystallinity, which is expressed in the expansion of the lines of 0.338; 0.327 nm.

Figure 5 show that in sample No. 2 enriched with molybdenum oxide, the content of $CaMoO_4$ and nickel oxide decreases and the degree of crystallization of the zeolite is lower than in sample No. 1. In catalyst No. 3 with an excess of nickel oxide, the crystallinity of the zeolite structure is sharply reduced, this is manifested by a decrease in the intensity of the diffraction lines and their considerable expansion. The amount of phase and the degree of crystallinity of $CaMoO_4$ are noticeably reduced. In general, the most intense lines appear in the roentgenogram of crystalline calcium molybdate: 4.71; 3.07; 3.09; 2.87; 2.61; 2.25; 1.92; 1,864; 1.628; 1.585; 1.563 Å.

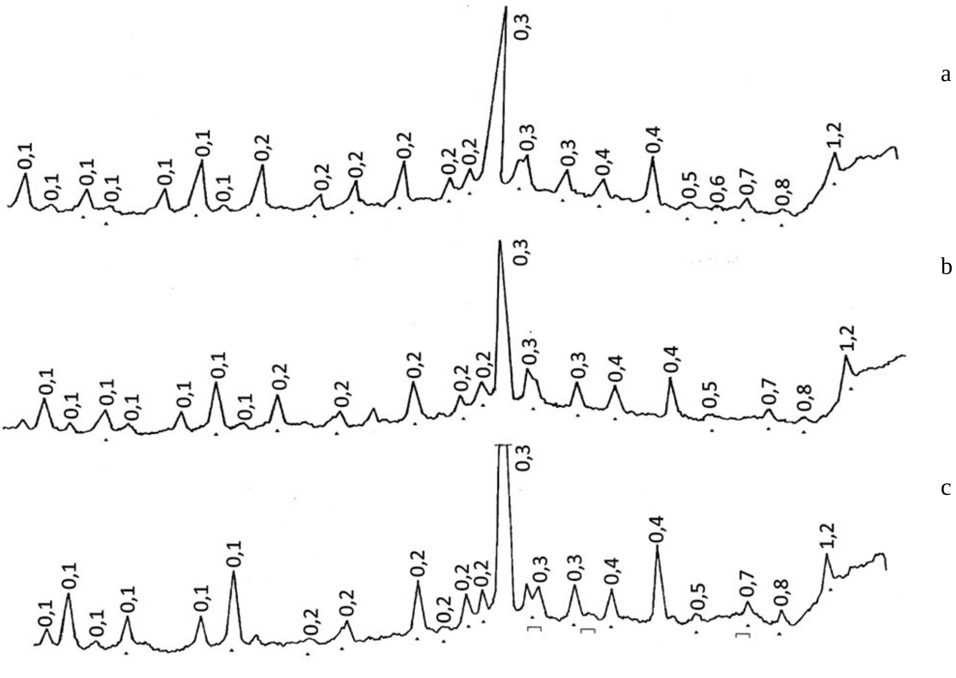

Figure 5 – Radiographs: a) Catalyst (No.1) - NiO: MoO_3 1: 1;
b) catalyst (No. 2) - NiO: MoO_3 1: 2; c) Catalyst (No.3) - NiO: MoO_3 2: 1

The presence of nickel molybdate, found earlier by ESR, can not be determined by X-ray diffraction, in view of its high dispersion and superposition of reflexes. However, molybdate of nickel is more or less present in all samples. The spinel structure of nickel aluminate was not found in the samples studied. According to the EDS, calcium molybdate exhibits acidic properties, so in the catalytic system it can serve as an isomerizing component. In Figure 5. X-ray diffraction patterns of molybdate nickel deposited on a thermoregenerated and activated zeolite are given. The catalyst was prepared by depositing $NiMoO_4$ on CaA, grinding the system to a powdered state (100-120 mesh), followed by transfer to a paste-like mass, its shaping into extrudates, drying and calcination.It follows from the X-ray diffraction pattern that the finished catalyst consists exclusively of $NiMoO_4$ and a thermoregenerated CaA zeolite. The results of the EDS and the thermograms of the catalyst showed no interaction of $NiMoO_4$ with CaA in this system Elimination of the interaction of the catalyst components - $NiMoO_4$ and CaA - shows their inherent high catalytic properties in redox and acid-base catalysis.

Conclusion. It was found that nickel molybdate has simultaneously hydrogenating, isomerizing, cleaving, hydrodesulfurizing, hydrodenitrogenating and other properties. The catalyst prepared by deposition of $NiMoO_4$ on zinc aluminate showed high results in the hydrogenation and isomerization processes.It was found that the $NiMoO_4$ catalyst on $ZnAl_2O_4$ is polyfunctional. At the same time, deep hydrogenation, isomerization, dehydrocyclization, cleavage and other reactions take place. A catalyst $NiMoO_4$ on $BaAl_2O_4$ manifests in these processes a greater degree of basic properties than acidic ones.Therefore, on this catalyst, deep hydrogenation reactions of hydrocarbons and, in particular, organo-nitrogen compounds of basic character, mainly take place.

Thus, structural studies of the spent CaA zeolite with salts of the active phase of nickel and molybdenum deposited under different thermal conditions have shown that it can be used as a solid carrier for the production of nickel-molybdenum catalysts with additives (promoters).In this case, the catalytic activity of the zeolite can be controlled by selecting it within the pore volume and composition.

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Резюме

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НИКЕЛЬ ЖӘНЕ МОЛИБДЕН ҚОСЫЛЫСТАРЫМЕН БЕЛСЕНДІРІЛІП ТЕРМОРЕГЕНЕРАЦИЯЛАНҒАН CaA-ТҮРІНДЕГІ ЦЕОЛИТТІ ЗЕРТТЕУ ЖӘНЕ ҚОЛДАНЫЛУЫ

Белсенді никель және молибден қосылыстарын пайдалана отырып CaA-цеолитін терморегенерациялау қарастырылады. Осы құрамдас катализаторлардың қыздыруға әсері зерттелінеді.

Түйін сөздер: катализатор, терморегенерация, адсорбент, цеолит, қолдану, араластыру, термиялық талдау, қыздыру, хемосорбция.

Резюме

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ИССЛЕДОВАНИЕ ПРИМЕНЕНИЯ АКТИВНЫХ ФАЗ НИКЕЛЯ И МОЛИБДЕНА НА ТЕРМОРЕГЕНЕРИРОВАННОМ ЦЕОЛИТЕ CaA

В этой работе был проведен процесс астивных фаз соединений никеля и молибдена на терморегенерированном цеолите CaA и изучены полученные на их основе каталитические системы

Ключевые слова: катализатор, терморегенерация, адсорбент, цеолит, использование, термический анализ, хемосорбция.