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REGENERATION AND CATALYTIC PERFORMANCE OF NI-MO-AL-HMS-H-BENTONITE CATALYST IN HYDROGENATION OF AROMATIC HYDROCARBONS

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Abstract. *Introduction.* The physico-chemical and catalytic properties of the bifunctional catalyst Ni-Mo-Al-HMS-H-bentonite were investigated in the hydrogenation of a model mixture of 2-methylnaphthalene and dibenzothiophene. *This study aimed to* compare the properties of fresh and regenerated catalysts and evaluate their efficiency in this reaction. *Results and discussion.* Catalyst physico-chemical parameters were analyzed by X-ray photoelectron spectroscopy, temperature-programmed hydrogen reduction, nitrogen adsorption-desorption analysis and thermogravimetric analysis. It was established that nickel and molybdenum are mainly present on the catalyst surface in oxide and sulfide forms that determine its catalytic activity. Textural analysis showed that the catalyst possesses a well-developed mesoporous structure with a monomodal distribution of pore sizes. After the catalytic reaction and regeneration, a decline in the textural characteristics were evaluated. Catalytic tests were carried out at 260°C, hydrogen pressure of 6 MPa and reaction time of 5 hours. The fresh catalyst maintained stable activity for four reaction cycles, while the regenerated catalyst demonstrated high efficiency for three subsequent cycles. *Conclusion.* The obtained results confirm the potential application of the Ni-Mo-Al-HMS-H-bentonite catalyst in hydrogenation processes of aromatic and sulfur-containing compounds.

Key words: mesoporous aluminosilicate, activated bentonite, bifunctional catalyst, Ni-Mo, model mixture

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1. Introduction

A substantial reduction in sulfur and aromatic compounds in petroleum products has become necessary due to the tightening of environmental standards for motor fuel quality. Sulfur-containing compounds, such as dibenzothiophene and its derivatives, produce sulfur oxides during combustion and must be removed from petroleum fuels. Therefore, the removal of these compounds is of considerable importance in contemporary petroleum refining [1]. Nowadays hydrodesulfurization is the most widely employed and effective industrial method for sulfur removal from petroleum fractions. This process is based on the catalytic hydrogenation of sulfur-containing compounds, followed by cleavage of the C-S bond [2,3].

The most widely used hydrodesulfurization catalysts are Ni-Mo and Co-Mo systems supported on oxide or aluminosilicate carriers. The high catalytic activity of these systems is attributed to the formation of an active Ni-Mo-S sulfide phase. This phase promotes both the hydrogenation of aromatic compounds and the cleavage of C-S bonds in sulfur-containing molecules [4]. Activity and selectivity of such catalysts strongly depend on the structure of the active phase, the metal particle dispersion and the characteristics of metal-support interactions [5,6].

The use of mesoporous aluminosilicate materials as supports for hydrotreating catalysts has generated particular interest. Such materials are notable for their large surface area, highly developed porosity, and the ability to tune surface acidity. These properties enable high dispersion of active metal components and facilitate reactant access to the catalytic sites [7].

Despite extensive studies on Ni-Mo catalysts, their stability and regeneration under hydrogenation and hydrodesulfurization conditions remain relevant. During operation, catalysts may undergo deactivation due to coke formation, agglomeration of active particles, and changes in the textural characteristics of the support [8]. In this regard, the comparative study of fresh and regenerated catalysts remains of considerable interest. It provides insight into the effect of the catalytic process on catalyst structure.

This work focuses on investigating the physico-chemical and catalytic properties of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalysts in the hydrogenation of a model mixture of 2-methylnaphthalene and dibenzothiophene. Dibenzothiophene was selected as a representative sulfur compound, since middle distillates mainly contain its alkylated derivatives [9]. The novelty of this work lies in the use of a combined Al-HMS-H-bentonite support containing activated bentonite from the Tagan deposit. This approach contributes to the development of catalytic materials based on Kazakhstan's significant bentonite resources. Particular attention is devoted to the state of active metal sites, the textural characteristics of the catalysts, and the evaluation of their catalytic activity, as well as to the effect of the regeneration process on the performance of the catalytic system.

2. Experimental part

Al-HMS mesoporous aluminosilicate with a Si/Al = 10 was obtained by a templating method using hexadecylamine. Tetraethyl orthosilicate and aluminum sec-butoxide were used as the sources of Si and Al, respectively. The resulting precipitate was separated by centrifugation, dried, and subjected to thermal treatment.

The catalysts synthesized by incipient wetness impregnation of the Al-HMS-H-bentonite support with aqueous solutions of $Ni(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, where activated bentonite was used as a secondary support. The obtained catalysts contained 5 wt.% Ni and 5 wt.% Mo. After mixing the solutions with the support, the samples were dried and subjected to thermal treatment.

The state of the metal centers in the catalysts was investigated by X-ray photoelectron spectroscopy (XPS) using a Nexsa G2 spectrometer (Thermo Scientific) and by hydrogen temperature-programmed reduction (H_2-TPR) by a Micromeritics AutoChem 2910 system. The textural characteristics of the synthesized samples were determined from nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics TriStar 3000 analyzer. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, while the total pore volume and pore size distribution were determined using the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TGA) of the bifunctional catalysts was carried out using a Mettler Toledo TGA/SDTA 851e instrument in an air atmosphere over a temperature range of 30-1000°C with a heating rate of 10°C/min.

The hydrogenation of aromatic compounds was studied using a model mixture. The mixture contained 9 wt.% 2-methylnaphthalene, 300 ppm dibenzothiophene (DBT), and 91 wt.% n-hexadecane. Before the experiments, the catalysts were activated in a flow reactor at 400°C in a H_2S/H_2 stream (10 vol %) for 5 hours with a heating rate of 4°C/min. After the hydrogenation reaction, the catalyst was regenerated in a muffle furnace in an air flow at 500°C for 5 hours with a heating rate of 3°C /min. The reaction was carried out in a high-pressure reactor at 260°C for 5 hours under a hydrogen pressure of 6 MPa. After the reaction, the products were examined using gas chromatography-mass spectrometry.

3. Results and discussion

The state of the active metal centers in the Ni-Mo-Al-HMS-H-bentonite catalyst was analyzed by XPS (Figure 1).

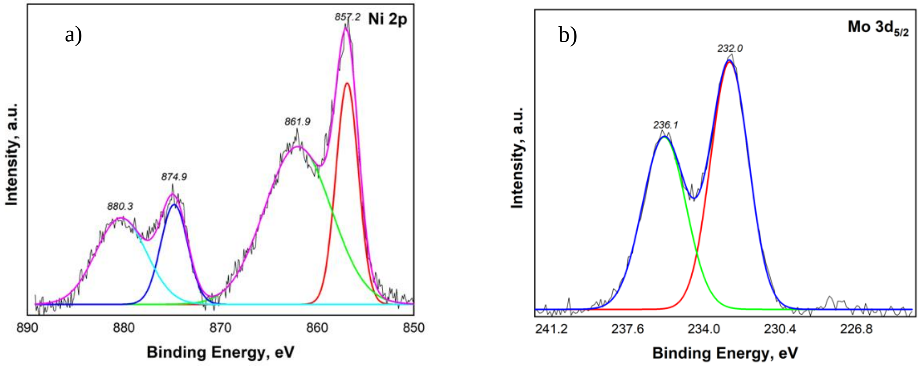

Figure 1 – XPS profiles corresponding to Ni 2p (a) and Mo 3d (b) for the bifunctional Ni-Mo-Al-HMS-H-bentonite catalyst

Analysis of the Ni 2p spectrum reveals the presence of two spin–orbit doublets (Figure 1a). The main Ni $2p_3/_2$ peak is observed at 857.2 eV with a satellite peak at 861.9 eV, while the Ni $2p_1/_2$ peak is located at 874.9 eV with a satellite signal at approximately 880.3 eV. The Ni $2p_3/_2$ peak corresponds to nickel oxide (NiO), indicating the presence of nickel in the oxidized Ni^{2+} state [10]. The presence of characteristic satellite peaks further confirms the oxide form of nickel.

The Mo 3d signals are displayed in Figure 1b. The obtained spectra exhibit two main peaks corresponding to the Mo^{4+} and Mo^{6+} oxidation states. The signals observed at binding energies around 232.0 eV and 236.1 eV are identified as MoS_2 and MoO_3 species, respectively [11]. This indicates the presence of molybdenum in both sulfide and oxide forms in the catalyst.

Metal-support interactions were investigated by H_2-TPR. The H_2-TPR curve of the Ni-Mo-Al-HMS-H-bentonite catalyst illustrates three peaks associated with different stages of reduction of the metal phases (Figure 2).

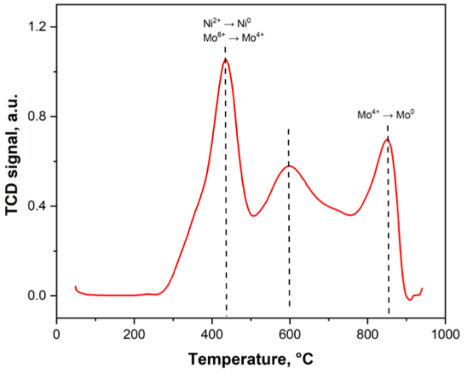

Figure 2 – H_2-TPR curve of the Ni-Mo-Al-HMS-H-bentonite catalyst

In Figure 2, the peak around 435°C is attributed with the reduction of NiO and MoO_3 oxides exhibiting high reducibility, corresponding to the transformation of Ni^{2+} to Ni^0 and Mo^{6+} to Mo^{4+} [12]. The peak at 600°C is associated with stronger metal-support interactions, indicating enhanced stability of the metal phases. A high-temperature peak at around 852°C is associated with the reduction of hardly reducible molybdenum species. It may correspond to the transformation of Mo^{4+} to Mo^0. The presence of this peak indicates the high thermal stability of the catalyst. Further, to evaluate the effect of the hydrogenation of aromatic compounds on the physico-chemical properties of the catalyst, a comparison of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite samples was performed.

The catalyst's textural characteristics were studied by analyzing the BET surface area, pore volume, and average pore diameter. These parameters play an important role in the formation of active sites and the accessibility of reactants to the catalyst surface. The obtained results are presented in Figures 3 and 4.

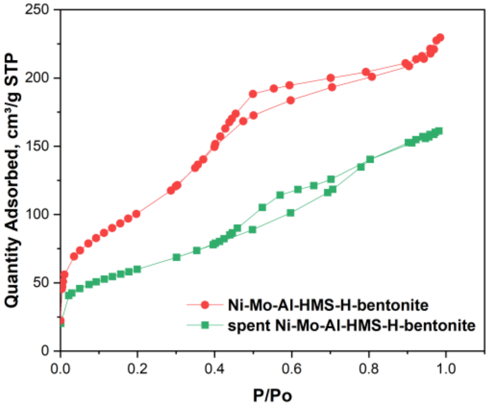

Figure 3 – N_2 physisorption isotherms of fresh and regenerated catalysts

An analysis of the textural characteristics of the Ni-Mo-Al-HMS-H-bentonite system was conducted using nitrogen physisorption. As shown in Figure 3, both fresh and regenerated samples exhibit type IV adsorption-desorption isotherms according to the IUPAC classification. The distinct H4 hysteresis loop observed for these materials serves as evidence of their mesoporous nature. The steep rise in adsorption within the 0.4-0.8 P/P_0 region can be attributed to the filling of mesopores via capillary condensation [13]. A comparative analysis reveals that the regenerated catalyst shows a significant decline in nitrogen uptake relative to its fresh counterpart. This reduction points to a partial degradation of the porous structure or a loss of surface area, likely resulting from the harsh conditions of the catalytic reaction.

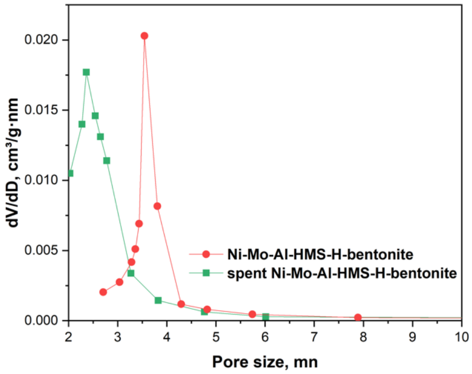

Figure 4 – Pore size profiles of fresh and regenerated catalytic materials

Figure 4 shows the pore size profiles of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalysts. The distribution is monomodal and lies within the mesopore region (Figure 4). The fresh catalyst is characterized by a maximum at 3.46 nm, whereas the regenerated sample exhibits a shift of the maximum toward smaller pore sizes, 2.36 nm, along with a decrease in peak intensity (Table 1).

Table 1 – Textural characteristics of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalyst

Ni-Mo-Al-HMS-H-bentonite	Specific surface area (BET), m^2/g	Pore volume, cm^3/g	Average pore diameter, nm
Fresh	805	0.74	3.46
Regenerated	675	0.67	2.36

After regeneration, the BET of the catalyst decreases from 805 to 675 m^2/g, while the pore volume decreases from 0.74 to 0.67 cm^3/g (Table 1). The reduction in textural characteristics after regeneration is likely associated with partial pore clogging by carbonaceous deposits formed during the catalytic reaction [2].

The TGA curves of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalysts show a decomposition of the sample with rising temperature. The primary decomposition step is observed from 200 to 600°C and is associated with the removal of adsorbed moisture, residual organic compounds, and the decomposition of surface functional groups (Figure 5).

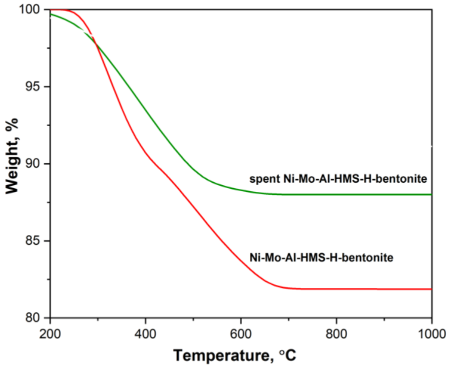

Figure 5 – TGA curves of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalysts

As shown in Figure 5, the fresh catalyst demonstrates a more weight loss compared to the regenerated sample. This may be attributed to the presence of a larger amount of surface species and residual organic compounds, whereas the regenerated catalyst demonstrates higher thermal stability [14].

The results of the study on the effect of sulfur-containing compounds on catalyst performance are presented in Figure 6 and Table 2. The catalytic performance was evaluated in the hydrogenation of a model mixture of 2-methylnaphthalene and dibenzothiophene at T = 260°C, $P(H_2)$ = 6 MPa, and a reaction time of 5 hours. The catalyst stability was examined over four consecutive cycles. It was found that after regeneration, the catalyst retains high activity for up to three cycles.

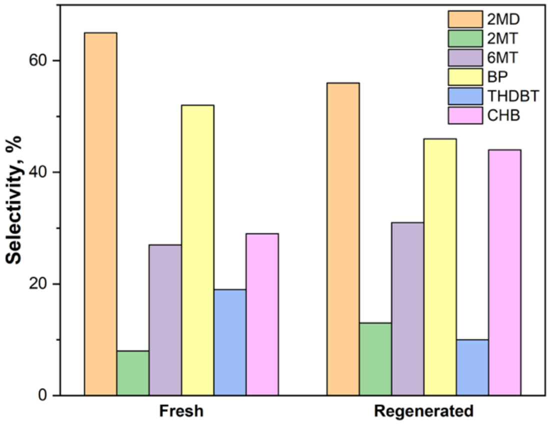

Figure 6 – Selectivity of hydrogenation products of a sulfur-containing model compound over fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalyst

Table 2 – Comparison of the performance of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalysts in the hydrogenation of a model mixture of 2MD and DBT

Ni-Mo-Al-HMS-H-bentonite	Conversion, %		Selectivity, %					
	2MN	DBT	**2MD**	2MT	6MT	**BP**	THDBT	CHB
Fresh	92	76	**68**	8	27	**52**	19	29
Regenerated	86	61	**56**	13	31	**46**	10	44
*Note: 2MN: 2-methylnaphthalene; DBT: dibenzothiophene; 2MD: 2-methyldecalin; 2MT and 6MT are 2-methyltetralin and 6-methyltetralin, respectively; BP: biphenyl; THDBT: tetrahydrodibenzothiophene; CHB: cyclohexylbenzene.								

The target products of hydrogenation are 2-methyldecalins and biphenyl. A comparison of fresh and regenerated catalysts revealed a decrease in both conversion and selectivity toward the target products after regeneration. The conversion of 2-methylnaphthalene decreases from 92 to 86%, while the conversion of dibenzothiophene decreases from 76 to 61%. At the same time, the selectivity toward 2-methyldecalins decreases from 65 to 56%, and the selectivity toward biphenyl in the hydrodesulfurization of dibenzothiophene decreases from 52 to 46%. Furthermore, the fresh catalyst yielded 63% 2-methyldecalin and 40% biphenyl. The corresponding values for the regenerated catalyst were 48% and 28%, respectively. The reduction in conversion and selectivity after regeneration may be attributed to partial changes in the state of active metal centers and a decrease in the catalyst textural characteristics. In addition, interaction of sulfur-containing compounds with active metal sites may lead to a decrease in their accessibility [15].

4. Conclusion

The physico-chemical and catalytic properties of fresh and regenerated Ni-Mo-Al-HMS-H-bentonite catalysts were investigated. Their performance was evaluated in the hydrogenation of a model mixture of 2-methylnaphthalene and dibenzothiophene. It was shown that the catalyst possesses a well-developed mesoporous structure and high catalytic activity. It was established that the catalyst maintains stability over four reaction cycles and, after regeneration, demonstrates high performance over three subsequent cycles. The obtained results confirm the potential of this catalyst for application in the hydrogenation of aromatic and sulfur-containing compounds.

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Conflict of Interest: The authors declare no conflict of interest.

РЕГЕНЕРАЦИЯ И КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ NI-MO-AL-HMS-H-БЕНТОНИТ КАТАЛИЗАТОРА В ПРОЦЕССЕ ГИДРИРОВАНИЯ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ

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Резюме: *Введение.* Физико-химические и каталитические свойства бифункционального катализатора Ni-Mo-Al-HMS-H-бентонит были исследованы в реакции гидрирования модельной смеси 2-метилнафталина и дибензотиофена. *Целью данного исследования* являлось сравнение свойств свежего и регенерированного катализаторов, а также оценка их эффективности в данной реакции. *Результаты и обсуждение.* Физико-химические характеристики катализаторов были изучены с использованием рентгенофотоэлектронной спектроскопии, температурно-программированного восстановления водородом, анализа адсорбции-десорбции азота и термогравиметрического анализа. Установлено, что никель и молибден преимущественно присутствуют на поверхности катализатора в оксидной и сульфидной формах, которые определяют его каталитическую активность. Текстурный анализ показал, что катализатор обладает хорошо развитой мезопористой структурой с мономодальным распределением пор. После каталитической реакции и регенерации было отмечено снижение текстурных свойств. Каталитические испытания проводились при температуре 260°C, давлении водорода 6 МПа и времени реакции 5 часов. Свежий катализатор сохранял стабильную активность в течение четырех реакционных циклов, тогда как регенерированный катализатор демонстрировал высокую эффективность в течение трех последующих циклов. *Заключение.* Полученные результаты подтверждают перспективность применения катализатора Ni-Mo-Al-HMS-H-бентонит в процессах гидрирования ароматических и серосодержащих соединений.

Ключевые слова: мезопористый алюмосиликат, активированный бентонит, бифункциональный катализатор, Ni-Mo, модельная смесь

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NI-MO-AL-HMS–H-БЕНТОНИТ НЕГІЗІНДЕГІ КАТАЛИЗАТОРДЫҢ АРОМАТТЫ КӨМІРСУТЕКТЕРДІ ГИДРЛЕУ ПРОЦЕСІНДЕГІ РЕГЕНЕРАЦИЯСЫ ЖӘНЕ КАТАЛИТИКАЛЫҚ БЕЛСЕНДІЛІГІ

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Түйіндеме. *Кіріспе.* Ni-Mo-Al-HMS-H-бентонит бифункционалды катализаторының физика-химиялық және каталитикалық қасиеттері 2-метилнафталин мен дибензотиофеннің модельді қоспасын гидрлеу реакциясында зерттелді. *Зерттеудің мақсаты* жаңа және регенерацияланған катализаторлардың қасиеттерін салыстыру, сондай-ақ олардың осы реакциядағы эффективтілігін бағалау болды. *Нәтижелер және талқылау.* Катализаторлардың физика-химиялық сипаттамалары рентгенофотоэлектрондық спектроскопия, сутек температуралық бағдарламаланған сутегімен тотықсыздану, азоттың адсорбция-десорбция әдісі және термогравиметриялық талдау арқылы зерттелді. Зерттеу нәтижесінде катализатордың активтілігін анықтайтын никель мен молибден оның бетінде негізінен оксидті және сульфидті күйде болатыны анықталды. Текстуралық талдау катализатордың жақсы дамыған мезокеуекті құрылымға ие екенін және кеуектердің мономодальды таралуымен сипатталатынын көрсетті. Каталитикалық реакция мен регенерациядан кейін текстуралық қасиеттердің төмендеуі байқалды. Каталитикалық сынақтар 260°С температурада, 6 МПа сутек қысымында және 5 сағат реакция уақыты жағдайында жүргізілді. Жаңа катализатор төрт реакциялық цикл бойы тұрақтығын сақтаса, регенерацияланған катализатор кейінгі үш циклде жоғары тұрақтылық көрсетті. *Қорытынды.* Алынған нәтижелер Ni-Mo-Al-HMS-H-бентонит катализаторының ароматты және күкіртқұрамды қосылыстарды гидрлеу процестерінде қолдану мүмкіндігінің жоғары екенін дәлелдейді.

Түйін сөздер: мезокеуекті алюмосиликат, активтендірілген бентонит, бифункционалды катализатор, Ni-Mo, модельді қоспа

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