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COMPARATIVE ANALYSIS OF THE PERFORMANCE CHARACTERISTICS OF INDUSTRIAL HYDROTREATMENT CATALYSTS

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ABSTRACT

Comparative analysis of hydrotreatment catalysts revealed notable differences in their performance levels. The study demonstrated that the industrial hydrotreating catalysts type-ACM (alumina–cobalt–molybdenum) and ANMS (alumina–nickel–molybdenum–silicate) manifest a significantly lower activity in the thiophene hydrodesulfurization reaction. Specifically, their performance characteristics were roughly two times lower compared to the most effective similar catalysts produced abroad. This was observed both before and after sulfidation with hydrogen sulfide, suggesting that while sulfidation does improve their performance, it does not bring them to the level of their more advanced samples produced abroad. The findings highlight the need for further optimization of catalysts to enhance their performance and competitiveness in industrial applications.

KEYWORDS

Catalyst, gasoline, oil refining, petrochemistry, sulfur, purification, diesel fuel.

Introduction

The growing demand for cleaner and more efficient energy sources has led to significant advancements in catalytic processes, particularly in the field of hydrodesulfurization (HDS). One of the key challenges in modern refining processes is the effective removal of sulphur compounds from petroleum fractions, as sulphur content in fuels significantly affects both their environmental impact and combustion efficiency. Catalysts play a central role in these processes, and their development is crucial for meeting stringent environmental standards while ensuring the production of high-quality fuels [1-3].

The paper focuses on the study of catalysts used for hydrodesulfurization, specifically examining the various types of catalysts and their effectiveness in removing sulphur from petroleum products. The analysis includes a comparison of both domestic and internationally manufactured catalysts, with a focus on their activity under different conditions, such as with or without prior sulfurization. The goal of this work is to ensure better understanding of the factors influencing catalyst performance and to identify the most efficient materials for hydrodesulfurization processes [4-8].

Through this study, we aim to provide valuable insights into the synthesis, activation, and application of catalysts, contributing to the development of more sustainable and eco-friendly refining technologies.

Materials and Methods

One of the significant sources of environmental and atmospheric pollution is distillate fuel that has not been adequately purified from sulfur and other impurities [9], [10], [11]. In the mid-20th century, industrialized countries began implementing regulations to limit the sulfur content in diesel fuel. This prompted the development of large-scale hydrotreatment capacities for distillate fuel. To produce similar fuels with sulfur content between 0.2–0.3 wt%, hundreds of major hydrotreatment facilities were commissioned in the United States, Japan, and European countries. However, these standards eventually became insufficient, and by the end of the last millennium, fuel quality requirements became significantly stricter [12-14].

Current sulfur content regulations in various countries require a significant reduction in this parameter—to as low as 10 ppm for straight-run gasoline used as reforming raw material, and to 0.01 wt% or less for diesel fuel. In addition, the previous limit on total aromatic hydrocarbons (no more than 20 wt%) has been replaced by stricter regulations on polycyclic aromatic hydrocarbons (no more than 6–10 wt%) and on cetane number, which must be 45 or higher.

Currently, the Fergana Oil Refinery produces diesel fuel with a sulfur content not exceeding 0.05 wt%. The hydrotreatment units use the imported NOR-463 catalyst (Japan), which is characterized by low mechanical strength, leading to frequent production shutdowns [15, 16].

In the reforming process units at industrial units at Bukhara Oil Refinery (BOR) and Fergana Oil Refinery (FOR), alumina–platinum–rhenium catalysts are used. These catalysts are implemented effectively in reforming processes, provided that the sulfur content in the feedstock does not exceed 1.0 ppm and nitrogen-containing compounds are virtually absent. However, the sulfur content in reforming raw material (straight-run gasoline) typically ranges from trace amounts up to 0.5 wt%.

At present, domestically produced hydrotreatment catalysts capable of reducing sulfur content to 1.0 ppm in refined gasoline and to 0.05 wt% or lower in diesel fuel are either virtually nonexistent or still in the development stage. The goal of our research is to develop a new, highly efficient, and mechanically robust catalyst to replace imported ones, as well as to establish a correlation between the physical and chemical properties, origin, and activity of the catalysts.

The hydrodesulfurization process of various petroleum products, which plays a crucial role in modern oil refining technology, continues to improve intensively, and its importance is steadily increasing.

The research aimed at developing highly active hydrotreating catalysts for distillate feedstocks was conducted using catalysts manufactured according to our recommendations, based on the results of physical and chemical studies and activity tests.

The research was based on the following questions:

1. Physical and chemical studies of the properties of catalysts at various stages of their synthesis, thermal activation, and operation, with the aim to find out their integrity with performance.
2. Investigation of the impact of modifying additives on catalyst activity.
3. Study of the effect of synthesis conditions on catalyst activity.
4. Examination of the influence of activation conditions (heat treatment, environment and temperature during heat treatment, reduction, and sulfidation) on catalytic activity.

Physical and chemical studies included:

1. Examination of the surface formation in catalyst.
2. Study of the adsorption characteristics (adsorption isotherms, holding volume, and heat of adsorption) of the catalysts.
3. Investigation of acidic properties, including total acidity and the acidity spectrum of the catalysts.
4. Determination of coke deposition and the degree of sulfidation of the catalysts during the testing of their catalytic activity.
5. Study of the formation of the active surface of the catalysts during the reduction process, aimed at understanding the genesis of the catalyst's active phases.
6. Derivative thermo-gravimetric analysis of catalyst phase formation and stability during heat treatment, also aimed at studying the genesis of the catalysts.

The methodology for physical and chemical studies of catalyst properties was developed earlier and is described in the works of [[7], [14]].

The results of physical and chemical studies, combined with data on catalytic activity, enabled the targeted synthesis of catalysts, ensuring the production of samples whose activity steadily increased.

For sulfiding the catalyst, a solution with a mass fraction of sulfur of 3% was prepared. Thiophene was used as a sulfiding agent. The essence of the process is to pass a high-sulfur component through a catalyst bed until hydrogen sulfide is released. The onset of hydrogen sulfide release indicates the transition of the oxide form of the catalyst to the sulfide form. Sulfiding was carried out in a flow-type unit at a temperature of 250 ° C. A series of experiments on hydrotreating the diesel fraction were carried out in a laboratory flow-type unit in the temperature range of 320 - 360 ° C with a step of 20 ° C, at a hydrogen feed rate of 6 l / h. The duration of the experiment was 1 hour, with preliminary activation in a hydrogen stream for 2 hours, the feed rate of the raw material was 8 ml / h. The main indicator for assessing the activity of the catalysts was the hydrodesulfiding capacity, i.e. the degree of purification of the hydrocarbon mixture. The degree of fuel purification at different process temperatures was determined by the difference in the sulfur content in the diesel fraction before and after hydrotreating. The sulfur concentration was determined by the accelerated sulfur determination method (GOST 1437-75). The essence of the method is to burn the oil product in a stream of air and capture the resulting sulfur dioxide and sulfuric anhydrides with solutions of hydrogen peroxide with sulfuric acid and titration with a solution of sodium hydroxide. The degree of purification of the diesel fraction was calculated using the formula:

$$\frac{C_{\text{н}}-C_{\text{к}}}{C_{\text{н}}} \times 100\% = \alpha$$

, where $C_{\text{н}}$ is the sulfur concentration in the unrefined fuel, $C_{\text{к}}$ is the sulfur concentration in the refined fuel

A study of the effect of hydrodesulfiding activity on the sulfided catalyst showed that the best result was achieved at a feed space velocity of 0.8 h -1 and T = 360 °C.

For comparison, a non-sulfided $CuNiMo/Al_2O_3$ catalyst was selected. The catalyst was tested on a diesel fraction with an initial sulfur content of 0.72 wt.%. The best result of hydrodesulfiding activity was achieved at a feed space velocity of 0.8 h -1 and T = 360 °C, the purification degree was 87%. The data on the activity of the sulfurized catalyst show that the sulfided catalyst exhibited greater hydrodesulfiding capacity at lower temperatures than the non-sulfided catalyst. The maximum purification degree was 84% with a residual content of sulfur-containing components of 0.33% by weight, which meets the requirements of EN 590. The developed catalyst can be considered as a catalyst in the process of secondary processing and improvement of the quality of petroleum fuel.

Results and Discussion

The synthesized catalyst samples were tested using three methods on three different types of raw materials.

1. The initial evaluation of catalyst activity was carried out in the hydrogenolysis reaction of thiophene using a modified method from BashNII NP [[7]]. All synthesized catalyst samples were tested using this method, including experiments both with and without prior sulfidation of the catalysts in a H_2 + H_2S stream.

2. A number of samples, representing the key stages in improving the catalyst synthesis and pre-activation methods, were tested in flow reactors under hydrogen pressure of 4.0 MPa with a feedstock volumetric flow rate of 1.0 hour^{-1}.A model representing a mixture of benzene and thiophene was used as the raw material, with a sulfur content corresponding to 0.5 wt.%. The applied methodology allowed for the evaluation of functional properties at the initial stage of catalyst operation (testing duration: 8 hours), including hydrodesulfurization, hydrogenation (hydrogenation of benzene to cyclohexane), isomerization (isomerization of cyclohexane to methylcyclopentane), and cracking activity. The analysis of hydrogenation products was performed using a chromatographic method based on a specially developed procedure.

The content of residual thiophene sulfur in the hydrogenation products was determined using a photo colorimetric method. At the same time, the effect of preliminary sulfuring with hydrogen sulfide on the catalysts' activity was studied.

3. A series of catalyst samples, characterized by the highest activity based on the results of the two methods described above, were tested on laboratory high-pressure flow reactors using straight-run gasoline with a sulfur content of 0.02% by weight and diesel fuel with a sulfur content of 1.02% by weight from Fergana Refinery. The testing duration for straight-run gasoline was 120 hours. Testing

conditions included pressures of 4.0 MPa and 2.0 MPa, with a volumetric feed rate of 3.0 and 5 hour^{-1} at temperatures of 300°C and 360°C. The residual sulfur content was determined according to GOST (State Standards) 13380-67. The fractional composition of the hydrogenation products was determined by chromatographic distillation.

Along with the newly synthesized samples, industrial catalysts such as aluminum-cobalt-molybdenum (ACM) type GO-70 (manufactured in Russia), aluminum-nickel-molybdenum silicate (ANMS), as well as catalysts from Union Oil of California (USA) N-6797 – T21 and several other samples were tested. During these tests on laboratory flow reactors, the conditions for introducing the catalysts into the process were also varied:

- Catalysts without preliminary reduction.
- Catalysts that were pre-reduced.

The starting point of the research was the comparison of the activity of industrial samples of ACM and ANMS catalysts, available to us, including the N-6797 Type 21 and NORM-463 zeolite-containing hydrofining catalyst (GO-70, Russia) from Union Oil Company of California (USA), as well as laboratory samples of ANM and ANMS catalysts (samples XAM-2 and XAM-3).

The characteristics of the tested hydrofining catalysts are presented in Table 1. The test results for the listed catalysts are shown in Table 2.

Table 1. Characteristics of hydrotreatment catalysts produced abroad

№	Name, type, brand of catalysts	Bulk weight, g/ml	The content in the catalyst, % by weight.					Specific surface area m^2/g	Remarks
			CoO	MoO_3	NiO	SiO_2	P_2O_5		
1	H-6797 Type 21 (USA Union Oil of California)	0,75	0,8	15,9	9,5	4,0	3,5	187	Si and P_2O_5 are determined analytically
2	NOR-463 (Japan)	0,70	3,01	14,6	-	0,4	4,58	220	Si and P_2O_5 are determined analytically
3	Aluminum–Cobalt–Molybdenum (ACM) (Russia)	0,78	4,5	12,5	-	-	-	164	FeO 0,21% NaO 0,1%
4	Aluminum-Nickel-Molybdenum (ANM) (Russia)	0,64	-	12,5	4,25	-	-	234	FeO 0,21% NaO 0,1%
5	Aluminum-Nickel-Molybdenum-Silicate (ANMS) (Russia)	0,72	-	12,6	4,9	7,7	-	242	FeO 0,21% NaO 0,1%
6	BASF M 880	0,65	4,8	10,6	-	-	-	315	
7	Harshow 400 T/E							309	
8	GO – 70 (Russia)	0,77	4-5	12-15	-	-	-	250	Na_2O – 0,08 Fe_2O_3 – 0,08

The data clearly show that the ACM and ANMS catalysts, as well as their laboratory similar samples (samples XAM-2 and XAM-3), exhibit approximately the same performance in tests both with and without preliminary sulfurization using a hydrogen-hydrogen sulfide gas mixture. The conversion rate of thiophene on these catalysts, with a feed weight flow rate of 2 hour^{-1}, was 16.0-20.3% and 31.0-31.5%, respectively.

An exception was the GO-70 catalyst. Regarding this catalyst, the thiophene conversion rate in tests without preliminary sulfurization was only slightly different from that of the ACM, ANM, and ANMS catalysts, at 21.0%. However, it increases sharply to 51.0% when the pre-sulfurized catalyst sample is tested, approaching the conversion levels seen in some foreign catalyst samples.

The catalyst samples from foreign companies are divided into two groups based on their performance. The first group, with average activity, includes catalysts from BASF, Harshaw, and NOR-463, with thiophene conversion rates ranging from 29.0% to 39.0% without preliminary sulfurization and from 37.4% to 42.0% after sulfurization. The second group, consisting of highly active catalysts, includes the "Union Oil" N-6797 Type 21, where the thiophene conversion rate without preliminary sulfurization ranged from 37.7% to 42.5%, and after sulfurization, it ranged from 56.9% to 63.5%.

Table 2. Results of comparative tests of industrial hydrotreatment catalysts

№	The catalyst	Pretreatment conditions of the catalyst				Specific surface area m²/g	Catalyst activity, % by weight.			Composition of coke deposits	
		Piercing			Blackening		Thiophene Conversion	Hydrogenation	Splitting	C %	S %
		Temperature, ºC	Time, hour	environment							
1	Al-Ni-Mo-Si	-	-	-	Blackened	242	31,5	0,127	0,012	0,42	0,28
2	Al-Ni-Mo-Si	-	-	-	-	242	16,0	0,108	0,031	0,87	1,41
3	Al-Co-Mo	-	-	-	Blackened	164	31,0	0,135	0,020	0,56	2,26
4	Al-Co-Mo	-	-	-	-	164	20,3	0,145	0,040	0,53	2,07
5	GO-70	580-590	12	-	Blackened	250	51,0	0,232	0,017	0,74	3,80
6	GO-70	580-590	12	-	-	250	21,0	0,136	0,037		
7	Harshaw	-	-	-	Blackened	220	42,0	0,205	0,034	0,27	3,53
8	Harshaw	-	-	-	-	220	39,0	0,176	0,026	0,76	3,42
9	BASF	-	-	-	-	315	29,0	0,137	0,013	0,99	2,15
10	NOR-463	-	-	-	Blackened	192	37,4	0,147	0,023		
11	NOR-463	-	-	-	-	192	36,0	0,180	0,018	0,84	1,74
12	H-6797 №21	-	-	-	Blackened	187	63,5	0,272	0,022	1,08	3,01
13	H-6797 №21	-	-	-	-	187	40,3	0,185	0,017	1,68	0,84
14	XAM-2	620	10	Air	Blackened	234	24,0	0,124	0,030	1,59	1,56
15	XAM-2	620	10		-	234	16,4	0,098	0,029	0,88	1,60
16	XAM-3	620	10	Air	-	213	16,2	0,141	0,028	1,57	2,13

It is noteworthy that different catalysts react differently to preliminary sulfurization with a hydrogen-sulfur hydrogen mixture. The ACM and ANMS catalysts increase their activity by 1.5 to 2 times after preliminary sulfurization, while the GO-70 increases its activity by 2.5 times. The “Harshaw” and NOR-463 catalysts show little change in activity after preliminary sulfurization, whereas the “Union Oil” N-6797 Type 21 catalysts increased their activity by approximately 50% after sulfurization. The reasons for the different responses of the catalysts to preliminary sulfurization, despite similar component compositions and total active component content (Table 1), may be related to differences in the phase composition of the catalysts, which include the active components and the alumina support, as well as the varying reactivity of the phases that make up the catalytic composition.

As demonstrated by the derivatographic studies [5] and further supported by the data discussed below, this is primarily a result of using different methods of synthesis and thermal activation for the examined catalysts.

The experimental data indicate that the activity of the industrial hydrofining catalysts, ACM and ANMS, is approximately twice lower than the activity of the best foreign samples tested, both when tested without prior sulfidation with hydrogen sulfide and after sulfidation in the thiophene hydrogenolysis reaction.

Conclusions

The findings of this study underline the significant impact of catalyst composition, activation methods, and sulfurization processes on the efficiency of hydrodesulfurization reactions. The comparison of various catalyst samples, both domestic and international, reveals that catalysts with proper activation and sulfurization treatments exhibit superior performance in reducing sulfur content in petroleum fractions. Specifically, catalysts that underwent preliminary sulfurization showed enhanced performance, with some foreign samples demonstrating significantly higher conversion rates compared to domestic ones.

The results suggest that while domestic catalysts, such as AKM and ANMS, perform well under certain conditions, they generally lag behind in performance characteristics when compared to the best-performing foreign catalysts. However, the right selection of synthesis and activation methods can potentially improve the efficiency of domestic catalyst systems. Further research into optimizing these processes could lead to the development of more effective catalysts for environmentally friendly and economically viable refining practices.

In conclusion, the study emphasizes the importance of continuous innovation in catalyst design and activation, with a focus on improving the environmental and economic aspects of hydrodesulfurization technology. The insights gained from this research can serve as a foundation for future advancements in catalyst development and refinery optimization.

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