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STUDY OF THE ACTIVITY OF SYNTHESIZED CATALYSTS IN THE REACTION OF HYDROGENOLYSIS OF THIOPHENE

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Annotation: The influence of the type of alumina carrier used on the activity of synthesized hydrotreating catalysts. In order to expand the sources of raw materials obtained by various methods for preparing the catalyst and studying its physicochemical characteristics. An important component for hydrotreating is γ - Al2O3. Monitor the carrier with high surface area and high thermal stability, its surface acidity.

Keywords: Catalyst, hydrotreating, aluminate-sulfonic acid, tablets, thiophene hydrogenolysis, heat treatment, aluminum oxide.

Introduction: As a carrier of industrial hydrotreating catalysts, aluminum oxide is used, obtained by shifting in proportions 1:1 “Cold” and “Hot” precipitation of aluminum oxide from an aluminate solution by rubbing with sulfuric or nitric acid. Initially, the precipitate is a gel-like substance, giving a blurry x-ray image. The gel-like primary sediment is usually aged in the temperature range of 40-800C. Aging conditions have a significant impact on the properties of the final product. After aging, the precipitate is filtered, washed and dried. The final stage of preparation consists of heating at a temperature of 6000C. During this operation, Al2O3 passes through various hydrated states.

Methods. In this case, the type of support used is important from the point of view of obtaining a catalyst with an optimal distribution of pore radii - a parameter that, as follows from the literature review, is currently receiving the greatest attention in the development of new hydrotreating catalysts.

Methodology of work and processing of experimental results.

From these types of ingredients, dough-like masses are prepared with a loss on ignition (LOI) of 80% (loss on ignition) at a temperature of 600°C. The mass was dried at temperatures of 100-120°C for 1-2 hours, then the temperature at an average rate of rise of 50°C/hour was brought to 320-350°C and the mass was kept at this temperature for 1.5-2 hours. Subsequently, the mass was crushed and mixed with graphite (4% by weight), sieved on sieves with a mesh size of 0.8 mm and tableted on a laboratory tablet machine with maximum force of the press tool.

The moisture content of the mass used for tableting was 6-8%, the size of the tablets was 5x5 mm. The tablets were heated at an average rate of temperature rise of 50-70°C/hour to 600°C and kept at this temperature for 6 hours. The mechanical characteristics of the prepared tablets depending on the heat treatment time are given in table. As can be seen from Table 3.3, no increase in strength is observed after 12 hour calcination.

A slight increase in strength and its decrease during prolonged heat treatment of aluminum oxide tablets is explained, in our opinion, primarily by the fact that the mass of aluminum oxide hydrate subjected to heat treatment at temperatures of 320-3500C has a low humidity of 6% (PPP at a temperature of 600 0C no more than 20%, a certain amount of aluminum hydroxide is converted into aluminum oxide.

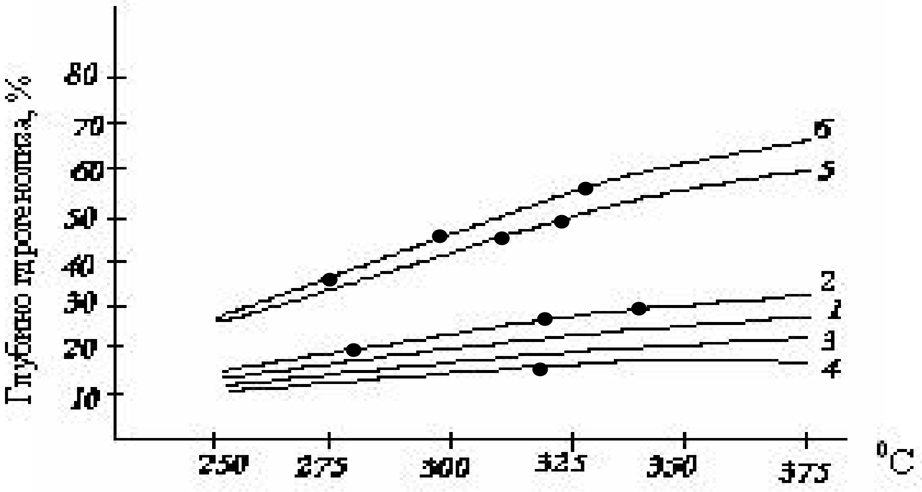
Mechanical characteristics of catalysts

№	**Enterprise manufacturer of aluminum oxide hydrate**	**Strength before calcination kg/tab.**	**Heat treatment time at 6000C**			
			6 hours		**12 hours**	
			Strength kg/tab.	**К***	**Strength kg/tab.**	**К***
1	Commodity Angren Kaolin	2	1	-	1	-

Tableting of such a mass is difficult due to the deterioration of the filling conditions; the resulting tablets, having a partially completed design, give an insignificant increase in strength as a result of calcination or do not give at all.

For these tablets, in contrast to prepared other carriers, an increase in strength is also observed while maintaining the heat treatment time.

The results of testing catalyst samples obtained using aluminum oxide of various porosities in the thiophene hydrogenolysis reaction are shown in Fig. 1.



Rice . The influence of the type of support used (Al2O3) on the activity of catalysts in the state of thiophene hydrogenolysis. 1 – BF – 1; 2 – BF – 2 a; 3 – BF – 2u; 4 – BF – 9; 5 – BF – 22b; 6 – BF – 18.

From the data in Fig. 1. It can be seen that the optimal solution for the three catalyst synthesis options considered was the use of weighted aluminum oxide with a bulk weight of 0.70 g/cm3. Although the increase in thiophene conversion on catalysts obtained on alumina of the indicated type exceeds the conversion values in the presence of catalysts synthesized on the basis of samples of alumina of other types by only 3-4% abs., this trend can be traced for all three synthesis options. At the same time, the hydrogenation activity also increases, more significantly than hydrodesulfurization, while the splitting activity remains practically unchanged.

Table. 2.

Increase in mechanical strength of catalysts over time

heat treatment (heat treatment time 10 hours)

№	Manufacturer of carrier of prepared samples of Al-Ni-Mo catalyst	Strength of tablets before calcination kg/table.	Heat treatment time for tablets at 6000C			
			Formative strength kg/table	K*	End strength kg/table.	K*
1	Ryazan Oil Refinery	8,3	10,0	1,20	34,0	4,09
2	Novokuibyshevsky NPK	7,5	8,4	1,12	28,0	3,73
3	Dneprodzerzhinsky H.K.	8,0	8,8	1,10	30,0	3,75
4	Ryazan Oil Refinery	4,8	5,8	1,20	24	5,0

K* – Strength growth coefficient – the ratio of the increase in strength of tablets after and before calcination.

Since, as will be shown below, the result of determining activity of catalysts in the reaction of hydrogenolysis of thiophene directly correlate with the results of testing catalysts in the hydrotreating process of real raw materials, the established fact of higher thiophene conversion on catalysts with heavy alumina was realized during the subsequent development of options for the synthesis of hydrotreating catalysts.

On the same series of catalyst samples that were studied from the point of view of the influence of the type of oxide used as a carrier aluminum, the effect of calcination temperature of dried compositions for catalytic activity. The purpose of these studies was to test the possibility of reducing the calcination temperature of catalysts in accordance with the patent data given in the literature review, and to select the optimal calcination temperature for the aluminum-nickel-molybdenum catalyst we are developing.

The feasibility of such studies, especially for the aluminum-nickel-molybdenum system, follows from the fact of the large variety of crystalline nickel-molybdenum phases and the temperature ranges of their existence in this case, compared with the aluminum-cobalt-molybdenum system, which, naturally, should be manifested in catalyst activity.

The dried compositions were calcined in the temperature range 450÷620 0C for 10 hours. The results of testing catalysts calcined at different temperatures are given in table. 3.5.

From the data in table. 3.5. It can be seen that the calcination temperature has a noticeable effect on the activity of the catalysts, and this dependence is most significant and is determined by the preparation method.

As optimal, using the example of arr. BF-2, the calcination temperature was determined to be 550 0C. Therefore, in subsequent stages of development of hydrotreating catalysts, heat treatment at both the stages of intermediate and final calcination was carried out at a temperature of 550 0C.

A particularly significant role of the pre-calcination temperature is visible in the case of the catalyst arr. BF-2. In this case, reducing the calcination temperature from 620 to 550°C led to a more than 2-fold increase in activity in the thiophene hydrogenolysis reaction. Based on this, we can conclude how much more important the preliminary thermal activation of ANM catalysts is, both in terms of temperature and duration of calcination. Moreover, this question, as can be seen from the data in Table. 3. has different significance for catalysts obtained by different synthesis methods and requires additional research.

It is known that modification of the support using additives can change the interaction with the active phase and thereby enhance the activity of the catalyst. The oxides K, Cr2 O3 B2O3, TiO2, Ca, Ba, Zn were used as modifying additives. The oxides of K, Ca and Ba, B2 O3, TiO2 were added with precipitation simultaneously with the active components into a suspension of aluminum oxide from the corresponding nitrates. Cr and Zn oxides are from acetates. A catalyst sample (sample BF.21) was also obtained, in which cesium oxide was introduced by impregnation of a calcined aluminum-nickel-molybdenum composition.

Table 3.

The influence of calcination temperature on the activity of catalysts.

№ п/п	Catalyst	Conditions for pre-treatment of catalysts			Specific surface, m¬2/g	Catalyst activity indicators Temperature 400 0C, pressure = 4 MPa o.s. = 10-1 hour			Composition of coke deposits	
		calcination								
		Temperature, ^0C	Time, hour	Wednesday		Thiophene conversion, %	Hydrogenation, %	Splitting, %	S %	S%
1	BF – 2	620	10	Air	234	15,5	0,098	0,029	0,88	1,60
2	BF – 2	550	10	Air	288	16,4	0,092	0,032	3,6	2,26
3	BF – 2	500	10	Air	272	18,0	0,095	0,033	0,66	1,61
4	BF – 2a	620	10	Air	245	19,0	0,172	0,031	1,62	2,25
5	BF – 2a	550	10	Air	238	23,3	0,115	0,026	1,22	0,98
6	BF – 2a	500	10	Air	282	22,0	0,122	0,022	0,24	1,40
7	BF – 2a	450	10	Air	270	17,7	0,095	0,044	-	-
8	BF – 9a	620	10	Air	107	18,3	0,158	0,017	1,17	4,07
9	BF – 9a	550	10	Air	-	38,0	0,178	0,028	-	-
10	BF – 9a	620	10	Nitrogen	117	18,3	0,163	0,021	0,92	3,71
11	BF – 9a	550	10	Nitrogen	-	42,0	0,166	0,020	-	-

Results: Zinc oxide at concentrations of 1.2 and 2.0% has a similar effect. The observed fact of the absence of influence of alkaline modifiers on the activity of the ANM catalyst contradicts the data of the work in which the author showed that low concentrations of an alkaline promoter, in particular sodium, increases the σ - acceptor and π - donor ability of catalysts. The author explains this effect by the fact that alkali metal ions deposited on the surface, interacting with the most electronegative centers, block them, which leads to an increase in the donor-acceptor properties of the catalysts. According to the mechanism of thiophene hydrogenolysis proposed in the work, in the act of catalysis, σ - and π - donor-acceptor interaction of the reagent occurs in the act of catalysis, then an increase in the indicated properties of the catalysts should be reflected in an increase in their activity.

The increase in the activity of the catalyst modified with boron and titanium oxide is explained by the fact that when modified with boric acid in the IR, deformation vibrations of AL-OH groups are observed, the intensity of which greatly decreases after calcination and additional absorption bands appear corresponding to vibrations of B-O bonds (1440-740 and 540 cm-1) and B-O (1190 cm-1 [75]. The simultaneous presence of acidic H2BO2 and basic AL-OH groups on the surface of a dried carrier containing up to 6% H3BO4 is explained by the extremely weak basicity of aluminum hydroxide and very weak acidic properties of boric acid.

X-ray diffraction revealed that the chemical interaction of boric acid and titanium oxide with aluminum oxide is accompanied by the formation of amorphous aluminum borates similar to a binary system. Crystallization in AL2O3 B2O3 begins at a temperature of 727 0C. The absence of endo effect at a temperature of 300 0C from the thermal decomposition of H3BO3 and Ti(OH)4 in the thermogram of a multicomponent carrier (Fig. 4.4, h i) indicates the interaction of aluminum hydroxide and boric acid, titanium hydroxide already at the stage of impregnation and drying.

The endo effect at a temperature of 295 0C and a number of blurred endo effects at temperatures of 250, 400-455 and 525 0C are due to the superposition of the formation of aluminum borates and titanium compounds with aluminum oxide on the thermal dehydration of aluminum hydroxide.

Modification with boric acid and titanium hydroxide leads to the formation of a carrier. When mechanically processing aluminum hydroxide with solutions of boric acid and titanium oxide, the carrier components dissolve at the beginning with the formation of a layer of aluminum hydroxide complexes and impurity ions. This creates more favorable conditions for in-depth interaction with H3BO4 and Ti(OH)4 and the formation of a uniform film of aluminum borates; titanium – aluminum oxide films on a calcined carrier.

Based on the data obtained, it can be concluded that modification of the support with boric acid and titanium oxide makes it possible to obtain a mechanically strong catalyst with a developed specific surface area of 237-210 m2/g.

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