

CHANGES IN THE COMPOSITION OF THE CATALYST DEPENDING ON THE PRODUCTION METHOD, ENVIRONMENT AND TEMPERATURE WHEN CALVING DIFFERENT ENVIRONMENTS

Salixova Ozoda Abdullayeva

Candidate of Technical Sciences, Associate Professor
of the Tashkent Institute of Chemical Technology

E-mail: ozodaxon.salihova@gmail.com

Sidikova Gulchekhira Abduljalolovna

Senior Lecturer, Tashkent Institute of Chemical Technology

E-mail: gulihonsidikova@gmail.com

ABSTRACT

In order to study the effect of the support on the activity of aluminum-nickel-molybdenum catalysts, samples were prepared using aluminum oxide (bulk weight 0.70 g/cm³). Samples were prepared by coprecipitation (sample BF-2a) and impregnation (sample BF-9a). The test results showed that samples prepared by impregnation of alumina have increased activity compared to catalysts prepared using standard alumina. In this case, samples calcined in a nitrogen environment have the greatest activity.

Keywords: influence of the carrier, activity, aluminum-nickel-molybdenum catalyst, thiophene, temperature, hydrogenating, calcination

ANALYSIS OF LITERATURE ON THE TOPIC

The activity of samples obtained by coprecipitation, according to test data, does not depend on the type of aluminum oxide in the initial period of operation. Catalysts obtained by coprecipitation have a larger specific surface area with a uniform distribution of active phases compared to catalysts obtained by impregnation. However, as part of the active phases in small pores is blocked by carbon deposits, their activity will decrease, and to varying degrees, depending on the structure of the carrier. The state of the active phases of the catalyst can be monitored by the catalyst saturation curves with sulfur during sulfidation. As can be seen from the figure, on samples BF-2 and BF-2a the initial rates of sulfur saturation are very close, however, the sulfur capacity of sample BF-2a is higher than that of sample BF-2. This suggests that the dispersion of the active phases of sample BF-2a is higher; therefore, an increase in the activity of the sample can be expected. BF-2a compared to mod. BF-2.

The initial rates of sulfur accumulation on samples BF-2 and BF-2a are virtually the same and do not depend on the medium during calcination. Obviously, during sulfurization with hydrogen sulfide in coprecipitated catalysts in the initial period, the dispersion of the active components has a lesser effect on the depth of sulfurization due to the larger surface area on which these phases are distributed. Therefore, in the initial period of work, the activity of the samples is the same.

METHODS

When comparing the curves of sulfur accumulation on catalysts obtained by impregnation, it is clear that already at the initial moment the rates of sulfurization of samples after calcination in air and in a nitrogen atmosphere differ significantly. Therefore, even in a short test cycle, differences in the activity of these catalysts appear.

Table 2. Dependence of acidity and activity of catalysts on the preparation method and processing conditions

No	Catalyst code	Temperature OC Calcination medium	Acidity mol/g	Spectrum of acid sites, kcal/mol	Hydrogenati on activity, %	Isomerizi ng activity, %	Trip activity, %
1	BF -9	620 air	0,069		12,0	0,03	0,001
2	BF -9a	620 N ₂	0,077		39,2	0,05	0,047
3	BF -9a	620 N ₂ 10 hours	0,078	>30	65,0	0,08	1,23
4	BF -2a	620 air 10 hours	0,13	>30 16,2 13,0	38,5	0,02	0,09
5	BF -2a	550 air 10 hours	0,11	30,3 23,0 12,4	94,7	0,07	0,32
6	BF -2a	500 air 10 hours	0,13	43,4 32,3 22,8	30,6	0,05	0,11

The effect of pre-calcination temperature was studied using the example of sample. BF-2a. The results of the study showed (Table 2) that with a decrease in the pre-calcination temperature, the activity of the BF-2a catalyst in the thiophene hydrogenolysis reaction increases, the hydrogenation and decomposition activity reaches a maximum at a pre-calcination temperature of 5500C, and the isomerizing activity increases slightly.

The catalyst calcined at a temperature of 4500C for 20 hours showed the greatest activity in the reaction of thiophene hydrogenolysis. However, intensive coke formation and a decrease in the specific surface area of the catalyst after 12 hours of operation are observed. Moreover, the activity of the catalyst in the reaction of thiophene hydrogenolysis stabilizes after 12 hours, while when calcined at temperatures of 500 and 5500C it continues to increase (Fig. 1).

Derivative graphical study of the phase composition of the sample. BF-2a showed that the concentration of nickel molybdenum phases and the MoO₃ - Al₂O₃ solid solution in it is higher than in the sample. BF-2. crystallization of the active phases on it occurs less intensely and does not depend on the medium during calcination.

When the temperature changes during calcination, the specific surface area of the catalyst passes through a maximum at a temperature of 500-5500C. With increasing temperature from 450 to 5500C, the specific surface area increases. Above a temperature of 5500C, the specific surface area decreases, probably due to the high degree of crystallization of the carrier.

Thus, reducing the temperature during calcination to 500-550°C prevents crystallization of the support and, consequently, the active phases of the catalyst.

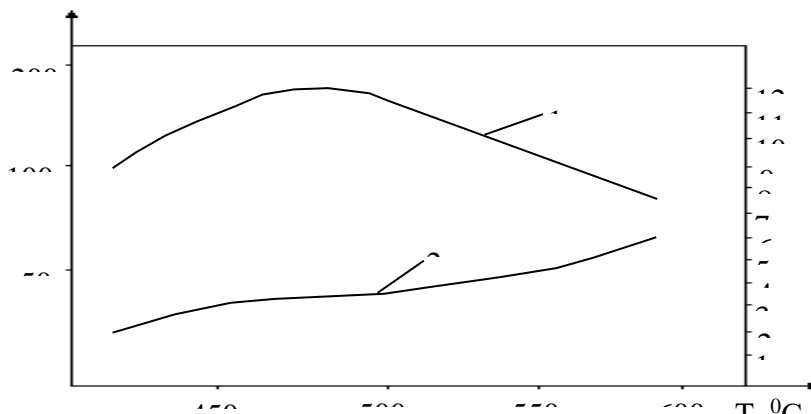


Fig.1. Dependence of changes in specific surface area and activity in the reaction of thiophene hydrogenolysis on the calcination temperature of the BF catalyst - 2 a. 1 - specific surface. 2 – activity in the hydrogenolysis reaction of thiophene.

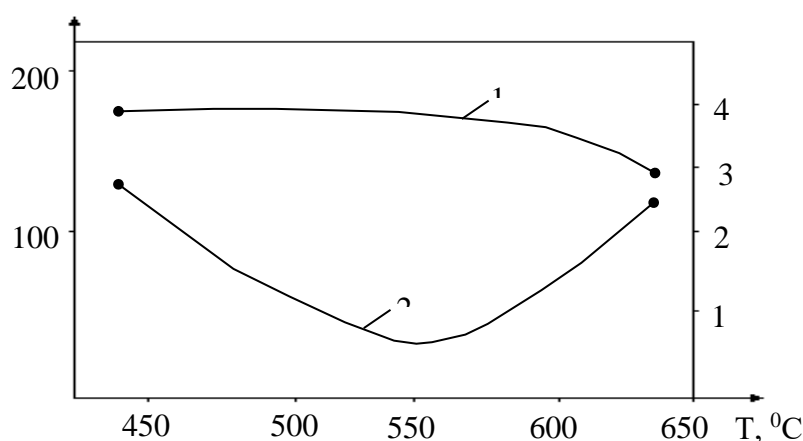


Fig.2. Dependence of the specific surface area and activity in the hydrogenolysis reaction of thiophene on the catalyst calcination temperature

BF - 18. 1 - specific surface area. 2 – activity in the hydrogenolysis reaction of thiophene.

The change in temperature during calcination also affected the acidic properties of the catalyst. First of all, it should be noted that the maximum acidity values of the sample. BF-2a corresponds to a calcination temperature of 500 – 600°C. From the results, it follows that catalysts calcined at 500 and 600°C have the same acidity, but the strength of their acid sites is different. It should also be noted that there is an antibacterial relationship between the acidity value and hydrogenation activity.

From a comparison of the activities of the sample. BF-9a and BF-2a it is clear that the sample exhibits the greatest activity in the hydrogenolysis reaction of thiophene. BF-9a, which, according to derivative graphic studies, has a higher concentration of nickel molybdate phases and the MoO₃-Al₂O₃ solid solution and a lower acidity value compared to the sample. BF-2, and the activity of arr. BF-9a increases mainly due to the increased concentration of the nickel molybdate phase in it.

In search of ways to increase the concentration of the nickel molybdate phase in the catalysts, the following were prepared:

1. Arr. BF-17, during the synthesis, in which aluminum oxide calcined at 6000C was impregnated with nickel nitrate, calcined in air and impregnated with ammonium paramolybdate;
2. Arr. BF-18, during the synthesis of which calcined aluminum oxide was impregnated with ammonium paramolybdate, calcined in air and impregnated with nickel nitrate. After impregnation at the second stage and drying, the samples were calcined in both cases in a nitrogen environment at a temperature of 6000C.

Regardless of the calcination temperature, the hydrogenation activity of this catalyst remains unchanged. The activity of the catalyst in the reaction of thiophene hydrogenolysis passes through a maximum corresponding to a calcination temperature of 5500C.

Methodology for carrying out work and processing experimental results. Obviously, this can be explained as follows. Impregnation of calcined aluminum oxide with nickel molybdate at $\text{pH} \leq 8$ and further calcination upon receipt of the sample. BF-18a leads to the formation of a uniformly distributed solid solution on the surface. $\text{NiMoO}_4 \cdot \text{Al}_2\text{O}_3$. In this case, the largest amount of nickel molybdate phase is formed at a temperature close to 5500C, where the crystallization process of the phases occurs to a lesser extent than at a calcination temperature of 6000C. This is evidenced by the results of determining the specific surface area and dispersion of aluminum oxide, which showed that upon calcination in the temperature range 450 – 5500C, the specific surface area of the catalyst and the dispersion of the carrier do not depend on the calcination temperature. The invariance of the specific surface area of the catalyst and the dispersion of aluminum oxide suggests that calcination at a temperature of 450-5500C mainly affects only the formation of the active phases of the catalyst. Calcination of the catalyst at 6000C leads to a decrease in the specific surface area and dispersity of aluminum oxide, and, consequently, the active phases, which is reflected in a decrease in activity in the thiophene hydrogenolysis reaction.

The dynamics of changes in the activity of the BF-18a catalyst in a 12-hour cycle (Figure 4.9.) shows that the hydrogenation activity depends little on the operating time of the catalyst for samples calcined at temperatures of 550 and 6000C. On catalysts calcined at temperatures of 450 and 5000C, hydrogenation activity decreases with increasing operating time. The activity in thiophene hydrogenolysis reactions increases with increasing operating time for all catalysts.

RESULTS

The above results indicate that the activity of the catalyst largely depends on the medium during calcination. A particularly strong dependence is observed on catalysts synthesized by the separate impregnation method. The data obtained showed that calcination in various environments apparently affects the concentrations of ions of active components in tetrahedral and octahedral coordination in the structure of the spinel support.

The concentration of ions in tetrahedral coordination is apparently higher during calcination in a nitrogen atmosphere than in air. Different positions of the ions of the active components

lead to a redistribution of Lewis and Brønsted acid sites, which affects the acidic properties of the catalyst.

According to this 1 and 2 Fig. When calcined in an oxidizing environment, molybdenum is predominantly in octahedral coordination.

CONCLUSION

We observed changes in the acidity of catalysts calcined in nitrogen and in air on all catalysts, regardless of the method of their preparation. Reduced acidity of the sample. BF-18a compared to mod. BF-9, synthesized in such a way that at the first stage of the synthesis, after impregnation with ammonium paramolybdate, they were calcined in air, and at the second stage, after impregnation with nickel nitrate, in nitrogen, due to the fact that in these cases, each of its atoms was probably introduced blocks two Brønsted acid sites. At the same time, the ratio of Lewis and Brønsted acidity increases. This proposal is confirmed by the distribution of the strength of acid sites in the sample. BF-18 and BF-22a, where mainly centers with an activation energy for pyridine desorption of 15-16 kcal/mol were found.

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