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Formation, Physicochemical, and Catalytic Properties of the Mo-containing Hydrotreatment Catalysts on Various Supports. IV: The Activity of the Catalysts for the Hydrotreatment of Black Oil

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Abstract—The activity and selectivity of the Mo–Ni catalysts prepared by the impregnation of supports (γ-Al_2O_3, hydrated titanium dioxide (HTD), and palygorskite–montmorrilonite clay (PMC)) are studied in the reactions of black oil hydrotreatment. The alumina support provides a higher catalytic activity in the hydrogenation of aromatics. The highest efficiency in desulfurization and demetalation of raw materials is achieved when hydrated titanium dioxide is used as a support. A low efficiency of the PMC-based catalyst is likely explained by the aggregation of the active component during hydrotreatment. The PMC support can be used as an additive to γ-Al_2O_3. Possible reasons for the dependence of the catalytic activity on the support are considered for various reactions.

INTRODUCTION

Fast growth of the technology for the hydrotreatment of petroleum fractions, the diversification of raw materials, and environmental requirements for the quality of the products stimulates diversification of the catalysts. The quality of products dictates the requirements of the catalyst activity in the reactions of C–S bond hydrogenolysis, hydrogenation, demetalation, and cracking that are dictated by the nature of raw material. Even in the processing of black oil of certain type, the use of a combination (packet) of 3–5 different catalysts in the reactor is reasonable [1, 2].

A difference in the catalytic properties of the supported Mo-containing sulfided catalysts is due to their chemical composition, different properties of various crystallographic elements of the layered MoS_2 and MoS_2-like structures, their morphology, and orientation relative to the surface of a support [3–8]. The nature of support, namely its hydroxyl coverage, which plays an important role in the genesis of the Mo/Al_2O_3 system [9, 10], can affect the structure of the molybdenum sulfide component of a catalyst. To extend the set of potentially usable supports and their components, it is of interest to study materials with various hydroxyl coverages. They can also be used as models for the study of the effect of support hydroxyl coverage on the genesis and properties of catalysts.

Earlier, we studied the hydroxyl coverage of γ-Al_2O_3, hydrated titania (HTD), and palygorskite–montmorrilonite clay (PMC), the interaction between these hydroxyls and the molybdate anions of an impregnating solution, the phase composition of catalysts, Mo dispersion, and the activity of the Mo/support and Mo–Ni/support samples in the test reaction of thiophene hydrogenolysis [11–13].

The goal of this work is to study the catalytic activity of the Mo–Ni catalysts on the above-mentioned supports in the hydrotreatment of fuel-oil residues (black oil and cracked residue).

EXPERIMENTAL

Catalysts containing 8.3 ± 0.5 wt % Mo and 3.0 ± 0.2 wt % Ni were prepared by the step-by-step incipient wetness impregnation of the supports with the solutions of ammonium paramolybdate and nickel nitrate. After impregnation, the catalysts were allowed to stay in the air for 24 h, dried at 110–120°C, and calcined at 450°C in the air for 5 h. Hydrotreatment was carried out in a pilot-scale flow setup at a reactant space velocity of 1 h^{-1}, 380°C (black oil) or 400°C (cracked residue), an H_2 pressure of 10 MPa, and an H_2 consumption of 1000 l per 1 dm^3 of a catalyst. Catalyst grains were 2–3 mm in size. Before feeding, the catalysts were sulfided by elemental sulfur for 2 h in an H_2 flow at 100–120°C, then the temperature was raised for 7–7.5 h. The duration of tests was 100 or 200 h. The content of S in a feed was 1 wt %, the content of the (V + Ni) metals was 40–45 ppm.

The products were sampled every 10–20 h, and the residual contents of S, V, and Ni were determined. The concentration of sulfur was estimated by burning in a calorimetric cylinder followed by the determination of the amount of sulfate anions in the washing water by titration with a solution of barium nitrate. The atomic adsorption spectroscopy (Saturn and AAS-1N spectrometers) was used to determine the amount of metals in a raw material and the reaction products using white spirit as a diluent. The reaction products and raw mate-

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rial were also probed by ^{1}H NMR on a Brucker WP-200 spectrometer with the working frequency of 200.1 MHz in a pulse regime using the quadrature detection. The spectra were processed according to a procedure described in [14]. The results were expressed as particular fractions of protons with respect to their overall number.

The starting and spent catalysts were studied by XRD on a DRON-3 diffractometer with Co and CuK_α irradiation. The amount of the condensation products deposited on the catalyst surface during hydrotreatment was estimated by burning method after first washing a spent catalyst out with a diesel fraction of the residues of a raw material and evacuation. A soluble fraction of the condensation products was extracted with benzene and studied by ^{1}H NMR spectroscopy after solvent removal.

RESULTS AND DISCUSSION

The study of the catalytic activity in desulfurization during 100-h tests in the hydrotreatment of black oil showed that the amounts of sulfur removed during this time from 1 cm^3 of the catalysts supported on HTD, Al_2O_3, and PMC are equal to 1.7, 1.4, and 0.6 g, respectively. The activity of the catalysts supported on HTD and Al_2O_3 was quite stable, and a decrease in the initial activity at the average (100 h) degrees of desulfurization equal to 75 (HTD) and 65% (Al_2O_3) was below 5–6%. The activity of the sample containing PMC decreased by 30% at an initial degree of desulfurization of 40%. Similar estimates were found for the activity of the samples in demetalation.

The intensive coking of the Mo–Ni/PMC catalyst is one of the possible reasons for its low efficiency. This assumption was confirmed by the low activity of this system in hydrogenation [13]. However, the estimated amount of the condensation products showed that coking is unlikely the main reason for fast deactivation. The amount of the condensation products in the spent catalysts based on HTD and Al_2O_3 was equal to ~30 wt %, whereas that in the catalyst based on PMC was only 14 wt %.

The XRD study of the spent catalyst showed that the degree of aggregation of MoS_2 in the Mo–Ni/PMC is much higher than the initial. This is evident from a substantial increase in the intensity of the strongest reflection (d/n = 6.15 Å) that is typical of this compound. The MoS_2 crystallites were not found in the Al_2O_3 and HTD supported catalysts. Hence, the main reason for the low efficiency of the catalyst based on PMC is the aggregation of the particles of the active component and a decrease in the active surface area during catalyst service. This is likely due to a weak binding of the active component with this support [12, 15]. Thus, the fractions of water-soluble molybdenum in the Mo/PMC, Mo/Al_2O_3, and Mo/HTD catalysts are equal to 70, 55, and 30%, respectively [15]. It is not improbable that a portion of the Ni promoting ions is removed during the growth of the MoS_2 packets.

These findings show that one of the methods to enhance the activity and stability of the hydrotreatment catalysts is to control the binding of the active component with the support surface. PMC is an inefficient support. However, it is of interest to study its applicability as an additive to the conventional γ-Al_2O_3 support (along with the promotion of the Mo/Al_2O_3 catalysts by zeolites and metallosilicates [16, 17]) because of its low price, great specific surface area, and high activity in the test reaction of thiophene hydrogenolysis [13]. For this purpose, the Mo–Ni catalyst based on the mixed support of 80% Al_2O_3 + 20% PMC was prepared and tested in the hydrotreatment of black oil. During a 200-h test, the degree of black oil desulfurization was higher than that of the catalyst based on Al_2O_3 by 5%. This effect was likely due to the same reason as the effect of the introduction of zeolites in the Al–Ni–Mo system. As shown in [16, 17], the addition of zeolites hampers the formation of poorly active Al–Mo compounds and an increase in the content of Mo–Ni structures that are most active in desulfurization. A change in the ratio of these structures seems to be due to weakened interaction between Mo and Al_2O_3 when an Si-containing additive was introduced into the system. Weakening took place, for example, when SiO_2 was added to Al_2O_3 [18]. This can be explained by a change in the nature of the hydroxyl coverage on the support, particularly by a decrease in the amount of the basic OH groups that are responsible for Mo binding to a support [11].

We can suggest that the introduction of an additive that weakens the interaction between an active component and a support will lead to two opposite effects on the desulfurization activity. On the one hand, this additive will increase the amount of Mo interacting with a promoter (Co or Ni) to form highly active structures. On the other hand, such an additive will decrease the dispersion of an active component. The first effect should increase the activity and the second should decrease the amount of Mo accessible to a reactant.

If the amount of the active Mo–Ni(Co) structures were only increased with an increase in the concentration of an additive, then we would expect the activity to increase to the level determined by the amounts of Mo and a promoter. If the effect of an additive only decreased dispersion, then a progressive decrease in the activity was the sole consequence. In fact, when these effects are simultaneous, the catalytic activity as a function of the additive concentration has an extremum. This explains an apparent increase in the activity when the mixed support Al_2O_3–PMC (see above) is used. That is why the activity function on the concentrations of zeolites and metallosilicates has a maximum as reported in [17, 19, 20]. The optimum concentration of an additive is 20–30%.

Because the sources of raw materials for hydrotreatment become more diverse, it is of interest to compare

the activity of the catalysts based on various supports in the hydrotreatment of secondary raw material (cracked residue). Cracked residue is heavier than black oil and it is enriched in aromatic compounds. During 200-h tests, the HTD-based sample provided higher desulfurization (by 5–10%) and demetalation (by 10–15%) than the catalyst on the aluminum oxide support.

Quantitative processing of the ^1H NMR spectra of the raw material and reaction products enabled us to conclude that, during the process, the signals from the protons of the individual and condensed aromatic rings dramatically change. The fractions of these protons among all protons in the reaction products and in the raw material differ by 15–25% at an overall fraction of protons in raw material of ~10%. The concentration of protons belonging to the individual rings is higher in the reaction products than in raw material and does not depend on the support nature. The hydrogenation rates for these structures are lower than the rates of their formation from more condensed systems. The amount of aromatic protons belonging to the condensed systems is lower in the reaction products than in the raw material. A most pronounced decrease is observed on the Mo–Ni/Al_2O_3 catalyst indicating its higher activity in the hydrogenation of these components.

Figures 1 and 2 show the relationship between the degrees of desulfurization and demetalation and the proton concentration in the condensed aromatic rings during the hydrotreatment of cracked residue. The maximum conversions are observed at the initial stage and the minimum conversions are at the final stage of the 200-hours tests. These findings indicate that the ratio between the active sites of the catalyst responsible for the hydrogenation and hydrogenolysis reactions depends on the support nature.

The ^1H NMR study of the soluble fraction of the condensation products deposited on the surface of the catalysts and the C/H ratio in the condensation products shows a higher activity of the Al_2O_3-based catalyst in the hydrogenation of aromatic systems. The ratio of the fractions of aromatic and aliphatic protons over the Mo–Ni/HTD and Mo–Ni/Al_2O_3 catalysts is equal to 5.4 and 4.5, respectively. The C/H ratio is equal to 1.2 and 1.1, and the insoluble portions in the condensation products are 70 and 48%, respectively, over these catalysts.

The control of the catalyst selectivity (i.e., a purposeful change in the ratio between the rates of reactions during hydrotreatment) is the most important condition for extending the set of the catalysts and solving the problem of environmentally clean fuels. A successful solution to these problems depends on the knowledge of the nature of active sites. Lesser attention is paid to the demetalation of the oil source. Demetalation is reduced to the adsorption of metal-containing components on the catalyst surface [15].

Different points of view exist concerning the nature of the active sites responsible for the hydrogenolysis of

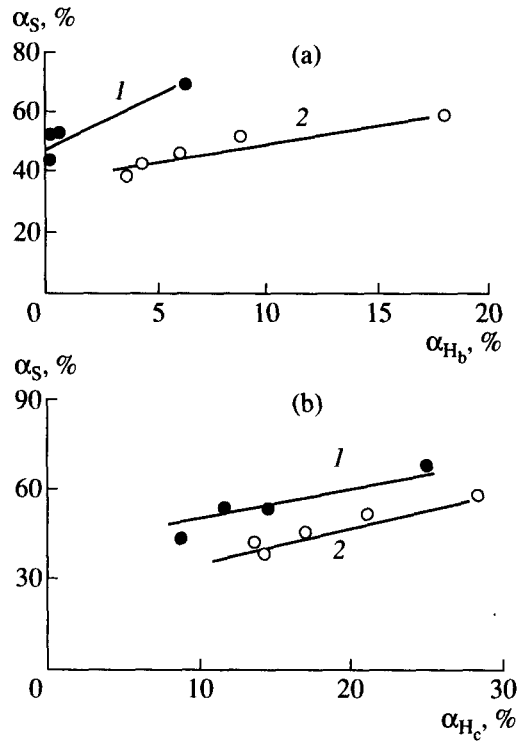

Fig. 1. The relationship between the degrees of sulfur removal (α_S) and hydrogenation in (a) bicyclic aromatic rings (α_{H_b}) and (b) more condensed aromatic structures (α_{H_c}) on (*1*) Mo–Ni/HTD and (*2*) Mo–Ni/Al_2O_3 catalysts.

S-containing compounds and hydrogenation of aromatic hydrocarbons. The question whether these reactions occur on the same or different sites remains open [21]. The ideas of the competitive chemisorption of the components of the reaction medium on the same sites [22, 23] and on the interconversion of the sites of hydrogenolysis and hydrogenation [23–28] are becoming more common. The most probable reason for this interconversion is believed to be a change in the ratio of the amounts of Mo and S in the catalytic system [23, 24, 26, 27]. As shown in [8], the Mo/S ratio affects the contributions from various crystallographic elements of the layered Mo-sulfided structures, including side and basal planes, as well as the relative catalytic activity in desulfurization and hydrogenation. One can suggest that the interconversion of the sites is accompanied by a change in the morphology of the active component particles. One of the factors that affect this change is the nature of a support [12, 29].

The data obtained in this work on the strengthening of one function of the catalyst and the weakening of another at the constant concentration of Mo while changing a support (Figs. 1, 2) can be rationalized on the basis of the assumptions of the interconversion of the active sites.

A stronger binding of the active component to a support is typical of the Mo–Ni/HTD catalyst; it is more

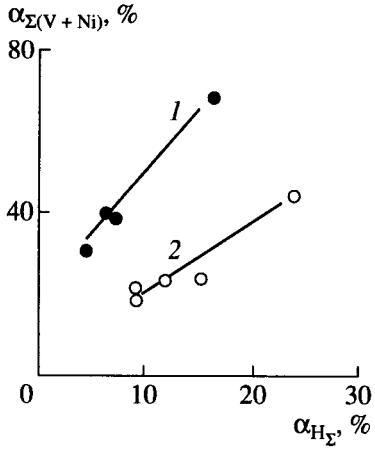

Fig. 2. The relationship between the degrees of the removal of metals ($\alpha_{\Sigma V+Ni}$) and the hydrogenation of the condensed aromatic rings on (*1*) Mo–Ni/HTD and (*2*) Mo–Ni/Al_2O_3 catalysts.

dispersed [12, 13], and hence, the side planes of its layered structures are less developed. The latter fact is unfavorable for the π-adsorption of the condensed aromatic compounds and results in a lower hydrogenating capability and an increase in the activity in desulfurization of the catalyst under the conditions of competitive chemisorption. According to [24, 26, 27], the high activity in desulfurization and, consequently, the higher concentration of H_2S in the reaction medium can additionally inhibit the hydrogenation of aromatic systems.

Molybdenum is more aggregated on the alumina support [12, 13]. This favors the formation of the side planes of the MoS_2 crystallites and the flat adsorption of aromatic hydrocarbons followed by their hydrogenation. The prevailing adsorption of the aromatic hydrocarbons that inhibits the access of the S-containing components to the active side planes is a possible reason for a change in the ratio of the activities in desulfurization and hydrogenation on going from HTD to Al_2O_3.

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