

Table 2. Results of tar hydrogenation (5 MPa; $\tau = 15$ min; tar : oil past-forming agent, 1 : 1; laboratory high-pressure setup)

Sulfur additive, wt % on a catalyst basis	Temperature, °C	Yield of liquid products with bp, °C			Total yield of distillate fraction, %	Gas + H ₂ O, wt %	Sludge, wt %	Losses, wt %
		to 180	180–250	250–320				
With no catalyst and sulfur additives	350	5.3	11.4	13.2	29.9	36.0	16.2	17.9
	400	7.8	15.3	24.0	47.1	36.3	9.1	7.5
	450	10.3	7.6	12.9	30.8	36.0	19.3	13.9
In the presence of a nanoheterogeneous molybdenum disulfide								
0.025% Mo + 0.03% S	350	1.3	15.2	42.0	58.5	22.8	14.5	4.2
	400	1.7	22.8	52.3	76.8	8.2	9.2	5.8
	450	1.2	11.5	38.8	51.5	26.4	14.2	7.9
0.05% Mo + 0.06% S	350	4.2	6.4	23.3	33.9	34.9	14.6	16.6
	400	14.7	18.7	31.7	65.1	10.7	18.5	5.7
	450	10.3	7.6	13.7	31.6	37.4	17.4	13.6
0.12% Mo + 0.09% S	350	4.2	6.4	23.2	33.8	40.0	17.8	8.4
	400	9.3	14.0	34.6	57.9	22.1	10.6	9.4
	450	5.3	7.1	12.6	25.0	45.0	18.9	11.1

Water- [2, 4] and oil-soluble [5] transition metal compounds can be used as precursors. Most often, monometallic molybdenum- or tungsten-containing precursors are used, which form MoS₂ or WS₂, respectively, in a hydrocarbon medium in the presence of a sulfidizing agent.

The hydrofining of highly aromatic fractions and residues in the presence of molybdenum disulfide synthesized in situ from aqueous solutions of a precursor has been widely studied. Extensive data on the catalyst morphology, the possibilities of its promotion, the optimization of emulsion compositions, etc., were obtained [6–8].

Petrukhina et al. [9] prepared in situ NoMoS and CoMoS catalysts in hydrocarbon feedstock by the decomposition of bimetallic water-soluble precursors and studied their catalytic properties in the hydrogenation and hydrodesulfurization of model compounds. The model feedstock was a 10% solution of bicyclic aromatic hydrocarbons in *n*-hexadecane and a 5% solution of dibenzothiophene (DBT) in benzene. It was found that an optimal promoter-to-molybdenum ratio in the catalyst was 0.25 : 1, and the test catalysts were highly active in hydrogenation and hydrodesulfurization reactions, including the recycling of raw materials.

Using coal hydrogenation as an example, Petrukhina et al. [9] demonstrated that a bimetallic Co/Mo-containing precursor (Mo₂Co₂S₄Cp₂(CO)₂, where Cp is cyclopentadiene) provided a higher conversion than a mixture of molybdenum and cobalt carbonyls.

Chunshan et al. [10] noted that the modification of nanoheterogeneous Fe-containing catalysts with the

addition of elemental sulfur (0.75–1.25% by weight on a catalyst basis) made it possible to increase the yield of total liquid products to 62.3–67.3% upon coal hydrogenation, as compared to that in the process performed in the presence of unmodified catalysts.

Along with the use of in situ nanoheterogeneous catalysts in an oil or coal paste-forming agent, the process of coal hydrogenation can be intensified by the preliminary ozonization of raw materials. Chunshan et al. [10] established a positive role of the preliminary ozonization of coal, which makes it possible to increase the yield of total liquid products by 13.3% upon hydrogenation, as compared with the yield of liquid products with the use of coal not treated with ozone. Kairbekov et al. [11] determined that preliminary ozonization for 60 min makes it possible to increase the yield of total liquid products by 44.8% and the yield of a fraction with bp to 180°C by 17.7% upon the subsequent catalytic hydrogenation of coal tar (5 MPa, 450°C, and in situ nanoheterogeneous Mo-containing catalyst in an oil paste-forming agent) in comparison with their concentrations in the initial tar.

In this work, we studied the catalytic properties of nonsupported molybdenum sulfide catalysts in the hydrogenation and hydrodesulfurization of semicoking coal tar from the Shubarkul deposit in order to obtain data necessary for intensifying the hydrogenation technology of tar conversion into raw materials for the production of needle coke, sulfur-free naphthalene, high-purity benzene for organic synthesis, and other chemicals.