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# TECHNOLOGY OF ORGANIC AND INORGANIC SUBSTANCES

# Investigation of a System of Protecting Layer for the Process of Hydrorefining Oily Distillates of Uzbekistan's Petroleum

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**Abstract**—Complex investigation is conducted, directed to development of contacting materials (forcontacts) and catalysts for the protecting layer in the process of hydrorefining petroleum distillates taking into account their specificity and extensively attracting local raw materials. Forcontact FZS-7 is developed which, besides the function of uniform distribution of crude material over the reactor section, diminishes tarring and performs, owing to low nickel content, mild hydrogenation of unsaturated compounds. The proposed kaolin-bset catalyst of the protecting layer with low content of molybdenum oxide works reliably with the residual crude material with high content of iron and displays high enough demetallization activity.

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Currently in Fergana's oil refining plant (FORP) is refined rather heavy hydrocarbon raw material from various fields in Uzbekistan, which is characterized by high content of paraffin, sulfur, and tarring compounds mixed with gas condensate. The refining scheme is defined by the local conditions: chemical composition of the petroleum distillates, nomenclature of demand by market petroleum products, and by technological potential of the facility for refining petroleum fractions.

Among the targeted processes in FORP a significant is producing basic lubricating oils with certain set of exploitation characteristics. The most problematic are enhanced colorization, compatibility with addition agents and low viscosity index. Correction of principal parameters of basic oils is performed at hydrorefining on G-24 installation where fractions of deparaffined distillate and deasphalted residue are treated in separate cycles. The tar-asphaltene substances colorizing petroleum products are mostly removed at deasphalting, but due to their volatility they contaminate oil distillates where they are undiserable due to high corrosion activity and deactivating effect on alumocobaltmolybdenum catalyst of hydrorefining. Design of the currently opertaing installation does not allow regeneration of deactivated catalyst directly in the reactor,

therefore when reactor os sealed by deposits the process shold be interrupted. From the reactor after cooling are removed ceramic rings and upper, the most wasted and damaged part of catalyst. Then fresh catalyst is loaded and on it the ceramic rings cleaned from edges and deposits are placed. Thus, the main mass of catalyst is used for long time without regeneration, and raw material often containing admixture of unsaturated compounds feeds into the zone of relative high temperature and active catalyst. Unsaturated compounds initiates formation of sealing products which leads to faster increase in pressure difference and poisoning of hydrorefining catalyst. To improve quality of lubricating oil and the process parameters it is reasonable to perform multilayer loading of catalytic paciage with additional forcontact and protecting catalyst layers.

Successful experimental-industrial testing of kaolin-phosphate forcontact (KPC) [1] in the reactor of Diesel distillate hydrodesulfrization in Fergana petroleum plant allowed considering of its application as front layer in treatment of heavier raw material. However, testing on a pilot-plant installation showed progressing grow of tarring components concentration in oil distillate, in residual fraction in particular, after contact with KPC under the process parameters analogous to those at the oil hydorefining (Table 1).

One probable reason for this observation is acceleration of polymerization reactions under the action of strong Bronsted acid centers [2] at lower hydrogen pressure compared to hydrodesulfurization of Diesel fuel. Really, testing the catalytic properties of KPC forcontact on a flow-type microinstallation in the temperature range 523-573 K revealed its ability of accelerating steric isomerization reactions of *a*-olefins and double bond migration into molecule followed by oligomerization. Yield of the products of intermolecular interaction of isomeric hexenes grows with temperature (Table 2), however, no surface coking was detected in the studied samples. Therefore for lowering the catalyst surface acidity excess to retard undesired reactions of to enhance hydrogenating function the KPC granules were impregnated with nickel compounds followed by thermal treatment. Studying showed that synthesis at lov pH values leads to dectrease in size of both large and small pores while impregnation of KPC by neutral solution increases fraction of pores 12-18 nm in diameter which leads to increase in sorption activity of the sample toward the largest test-molecules [3].Taking into account the coarse-pored structure and low specific surface of KPC, their impregnation conditions were taken to provide maximumm nickel concentration 1.3–1.5% inthe granules surface layer at the total NiO content 0.4–0.5% (sample FZS-7). IR spectrum of scrap from KPC granule surface showed decrease in the fraction of acid phosphites correlating with the change in acidity of the acid centers from  $pK_a > 1.5$  on the surface to  $pK_a < -3$  on the internal slice of granule. Modification of the forcontact with nickel compounds in neutral medium leads to relative increase in activity toward backbone isomerization of hex-1-ene and hydrogenation of forming unsaturated compounds.

Use of nickel salt solution with lower pH at impregnating KPC provides three-fold increase in concentration of surface acid centers with  $pK_a < -3$  and more homogenous distribution of nickel compounds in the bulk granule (sample FZS-1). This leads to obvious strengthening of polymerization function in a model

Sample		Deposits on contacts, %										
	Color, CNT units	Viscosity, cSt at 40°C	Viscosity index	Iodine number, iodine grams per 100 g of oil	Sulfur total, %	Ash resi- due, %10 <sup>-4</sup>	Cake	Tar				
Oil distillate fraction III												
	2.4	41.6	87.0	0.80	0.67	15						
KPC	3.7	42.9	89.3	0.82	0.65	13	5.8	1.2				
FZS-7	2.2	43.6	91.4	0.48	0.56	9	2.6	0.8				
FZS-1	5.2	40.2	90.7	0.74	0.66	12	11.2	2.0				
AKBM	2.0	39.2	94.3	0.35	0.43	7	4.2	1.8				
Oil distillate fraction III												
	4.5	61.0	93.5	0.35	0.91	23						
FZS-7	3.8	623	96.3	0.19	0.78	17	Did not define					
AKBM	2.3	53.6	104	0.03	0.73	12	Did not define					
Residual fraction												
	7.8	343.4	89.1	0.56	1.23	63						
FZS-7	7.2	366.2	90.1	0.32	1.18	51	11.4	3.7				
AKBM	5.2	296.0	99.5	0.13	0.97	29	6.9	4.5				

**Table 1.** Testing protecting layer contacts on a pilot-plant installation. Temperature 523 K, pressure 2 MPa, volume rate 2.0  $h^{-1}$ , hydrogen to raw material ratio 100:1

reaction and sharp fall in colorization of oil fractions at hydrorefining due to intense tarring. On the contrary, passing residual fraction through FZS-7 layer leads to decolorizatiun of product by 1-2 TsNT (colorimetric standard) units. Besides, occurs certain increase in hydrocarbon chain branching, probably owing to isomerization followed by hydrogenation of unsaturated components, which leads in some increase in viscosity (Table 1) and decreases freezing temperature by 1– $2^{\circ}$ C. Appearance of hydrogen sulfide in gas phase together with practical absence of C<sub>1</sub>–C<sub>5</sub> hydrocarbons attests proceeding of hydrogenation of the less stable sulfur compounds in oil fraction without C–C bond cleavage. Investigation of KPC samples and modified forcontact FZS-7 after their application to hydrorefining fraction III of oil distillate under the same condi-

**Table 2.** Comparative testing forcontact and catalyst activity in the model reaction of hex-1-ene conversion. Hydrogen pressure 0.001 MPa, volume rate  $0.5-0.05 \text{ h}^{-1}$ 

Sample	Vpore, cm3/g	T;K	Yield of reaction products, %					
	(Rpore, nm)		Cracking Isomerization		Hydrogena-	Oligomeri-		
				steric	carcass	tion	zation	
KPC	0.14	523	0	56.8	0.11	0	7.2	
	$(5 \div 6: > 10^4)$	573	0	57.4	0.63	0	12.6	
	(2 . 2, )	623	0.9	60.2	11.5	0	13.8	
FZS-7	0.21	523	0	37.2	19.3	0.3	2.1	
	$(7 \div 9: > 10^4)$	573	1.4	46.6	20.3	3.4	3.2	
	(,	623	1.6	49.7	23.3	7.9	3.7	
FZS-1	0.18	523	0	55.7	0.15	0	7.6	
	$(6 \div 8: > 10^3)$	573	0.05	58.0	0.76	0.9	14.3	
	(,,	623	1.0	62.2	9.7	2.4	20.3	
AK	0.31	523	0	11.5	4.6	0	9.0	
	$(2 \div 3: > 10^4)$	573	0.03	19.0	12.2	0	7.0	
	(,	623	1.5	20.6	13.4	1.0	10.0	
AB	0.58	523	0	55.8	9.3	0.2	1.4	
	$(2\div3:6\div8>10^4)$	573	1.0	52.3	14.8	4.5	2.8	
	(,	623	1.2	48.5	27.1	11.6	4.5	
AKB	0.68	523	3.4	44.3	13.4	0.5	1.5	
	$(4\div5; 7\div8 > 10^4)$	573	6.8	45.9	23.4	3.7	1.5	
		623	8.9	47.9	22.3	4.8	2.3	
AKM	0.68	523	0.37	20.2	10.9	2.4	2.5	
	$(4\div7; > 10^4)$	573	1.4	20.3	13.5	14.8	3.7	
		623	1.9	32.0	17.3	22.7	5.8	
AKBM	0.65	523	1.2	15.8	17.2	3.2	1.2	
	$(4 \div 8 > 10^4)$	573	1.5	17.3	19.2	15.4	1.6	
	```	623	3.3	21.1	19.9	30.6	2.8	

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**Fig. 1.** Changes in metal content: 1 – in residual fraction, 2 – after hydropurification on FZS-7 forcontact, 3 – on AKBM protecting layer catalyst

tion in a pilot-plant installation revealed decrease in content of dry cake from 5.76% to 2.6 and of tarasphalt substances extractable with benzene-alcohol mixture from 1.2% to 0.8%. On the FZS-1 forcontact surface was detected 11.2% of insoluble carboncontaining compounds. Comparison of decrease in concentration of metals in starting material and in the hydrogenizates (Fig. 1) with their distribution in "dry" cake and in extracts of caked samples allows to conclude that the forconacts partially trap alkaline and alkaline-earth metals, probably in the form of corresponding naphthenates dissolving in hydrocarbons. By the method of electron-sounding analysis we registered presence of sodium, potassium and calcium, mainly in ashed residues of oil fractions and in extracts of used up forcontact and catalyst of protecting layer (below). Concentration of typical catalyst poisons in the residual fraction, the vanadium, nickel and iron organic metallocomplexes, remains practically unchanged after passing oil through FZS-7 layer at hydrorefining, which attest low demetalliation function of this forcontact.

To avoid deactivation of cobaltmolybdenum catalyst in the process of work up heavy fractions, we prepared and studied a series of molybdenum-containing catalysts of protecting layer on the ground of clay minerals of Uzbekistan origin with by-products of local plants for their transformations. When carrier is prepared from bsevdobemit with 25% of kaolin, new very strong Si–O–Al bonds are formed between SiO<sub>4</sub> fragments of kaolinit and AlO<sub>6</sub> octahedrons of aluminum hydroxide. Optimal combination of strength and porous characteristics was achieved, in our opinion, with alumokaolin carrier modified with boric acid (Table 2).

The process of applying active metal from aqueous solution is significantly affected by state of hydroxyl shell of carrier, because change in solution pH is defined by dissociation of water molecules at the action of field strength of dominating aprotic adsorption centers. Study of acid-base properties of the smples dehydroxylated at 823 K showed that introducing kaolin to psevdobemit composition in strong acid medium enhances concentration of coordination-unsaturated aluminum ions on the surface of the calcined carrier, but on the other hand this promotes formation of Bronsted acid centers typical for alumosilicates [1]. Thus, the dehydroxylated alumokaolin carrier (AK) surface ears simultaneously fixed not mutually interacting strong aprotic and protic acid centers (pK<sub>a</sub>  $\leq$  -5) and weak aprotic basic centers. On immersing the AK sample into water occurs emphasized alkalization of the medium (pH from 5.9 to 6.8) rather than at the hydration of aluminum  $\gamma$ -oxide prepared by pseudobemit calcination at 873–923 K [4], that is, the ratio of primary (acid) and secondary (basic) Lewis centers is shifted in favor of the latter and surface pK<sub>a</sub> grows to 8.2. This is stipulated by formation of additional basic centers at the thermal decomposition of doped alkaline-earth

metal hydrocomplexes which in the process of plasticizing of the kaolin – bseudobemit mixture with nitric acid are washing out from kaolinit interpackage space, and further at thermal treating they are passed to the granule surface through capillary canals. De to irregular distribution of different type OH groups on the alumokaolin carrier surface, before formation of required monolayer, an "island" polymolybdate film is formed which contains up to 20% of water soluble molybdenum in the catalyst composition (AKM). The high content of water soluble mixed structures  $Mo^{6+}_{Td}$ –O–  $Mo^{6+}_{Oh}$  manifests itself as a bend at 33.3 kcm–1 in electronic diffuse reflectance spectrum, attesting weak enough interaction of active component with the carrier.

For strengthening granules and admitting protondonor property to surface of hydrorefining catalyst for facilitating desorption of hydrogenolysis reaction products, to the catalyst compositionis introduced boric acid. Modifying aluminum oxide with boric acid in the absence of kaolin leads to formation of carrier (AB) with high concentration of Bronsted acid centers (-8 < $pK_a < -4$ ) on its dehydroxylated surface. In the first moment its hydration proceeds presumably by basic type affording H+ ions to the surrounding medium and decreasing pH value from 5.9 to 5.6. Then pH grows to 6.0, which points to the presence of two hydroxyl centers of two sorts capable of ion exchange, as well as Lewis acid centers capable of binding active component by sorption. Acidification of the medium due to ion exchange between surface groups of AB carrier and ammonium para-molybdate water solution shifts equilibrium to the side of formation in solution of polymolybdate structures, while fraction of water-soluble oxidomolybdene clusters in the final sample achieves 15%.

Modified alumokaolin carrier with optimal  $B_2O_3$  concentration (AKB) the surface alumoborates formed after calcination at 773 K cover <sup>1</sup>/<sub>4</sub> of monolayer. In couple with alumosilicate structures they provide formation of bronsted acid centers in the pK<sub>a</sub> range from -4 to -1.5, regularly distributed on the carrier surface. At the contact of AKB with water the medium pH begins to change from 5.9 to 5.6, then becomes constant on 6.3 level, while pH of the carrier surface after hydration becomes equal to 7.2. Intoduction to this system of ammonium para-molybdate ammonia solution results in ion exchange reactions with surface structures and formation of Mo–O–Al, Mo–O–Si and Al–O–B–O–Mo bonds fied on the surface at thermal treat-

ment. Applying of molybdenum oxide does not change spectrum of distribution by strength of acid centers on the AKB carrier, but increases concentration of Bronsted acid centers on the catalyst surface (AKBM).

Extraction treatment of the prepared catalyst showed absence of molybdenum water-soluble forms, although the fraction of active molybdenum extracted by ammonia is high enough. IR spectrum of AKBM in KBr pellet registered with reference KBr containing equivalent amount of AKB for compensation of the carrier bands contain bands near 920 cm<sup>-1</sup>, which in conjunction with the data of electron diffuse reflectance spectroscopy evidences that molybdenum ions are in tetrahedral coordination and its significant part is in the composition of associates Mo<sub>Td</sub>-O-Mo<sub>Td</sub>, which are characterized by inflection point at 33.7 kcm<sup>-1</sup> Clear absorption band in the region of 40.0–43.3 kcm<sup>-1</sup> is assigned to formation of amorphous alumomolybdenborates revealing high catalytic activity in the process of hydrocracking of heavy petroleum [5].

Express testing of catalytic properties of the catalyst on a microcatalytic installation of flow type, on the samples not containing molybdenum in the temperature range 473 - 673 K predominantly occurs reactions of stereoisomerization and double bond shift into the chain of normal acyclic  $\alpha$ -olefin. Increase in concentration of acid centers pKa -5.6 leads to increase in the rate of formation of branced olefins due to backbone isomerization, but concentration of products of their hydrogenation decreases.

Hydrogenation of cyclohexene is accompanied with backbone isomerization with formation of methylcyclopentane and methylcyclopentenes. The same reaction products: cyclohexane, methylcyclopentane and various methylcyclopentene were formed bof in hydrohenation reaction and due to hydrogen redistribution in the experiments with inert gas. Although in the second case the products of backbone isomerization were formed in much less amount, their enhanced concentration on the samples with maximum acidity evidences unequivocally the principal role of strong acid centers in this process. We found that hydrogenating function of the catalysts correlates with concentration of water insoluble molybdenum, the maximal activity showed the catalyst on the carrier with the predominating strength of acid centers in the range -4.5 < pKa < -1.5. On the carries with stronger acidity (pKa below – 5) the hydrogenation reaction are less successful and in the hydrogenizate increases fraction of undesired products of oligomerization.

We performed continuously testing of optimal forcontact samples FZS-7 and of protecting layer catalyst AKBM on a pilot-plant installation of high pressure hydrorefining fractions III and resifual fraction af oil distillates. The forcontact FZS-7 improves characteristics on color and iodine number of oil fraction before their passing on the catalyst of hydrorefining. Depending on the process parameter, on the protecting layer catalyst AKBM stable decreases colorization and sulfur content, increases viscosity index at minimal decrease in viscosity, and effectively trapped iron and other metal ions.

### ABBREVIATIONS

- FORP Fergana oil refining plant,
- G-24 Installation for hydrorefining oil distillates,

KPC – Caolin-phosphate forcontact,

FZS-1 – Caolin-phosphate forcontact modified with nickel ions in acid medium,

FZS-7 – Caolin-phosphate forcontact modified with nickel ions in neutral medium,

AB - Alumoborate carrier,

AK – Alumocaolin carrier,

AKB - Alumocaolinborate carrier,

AKBM – Molibdenum-containing catalyst on the alumocaolinborate carrier.

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