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PRESULFIDING OF HYDROTREATING CATALYST BY ELEMENTAL SULFUR OUTSIDE OF THE REACTOR

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The ecological safety of petroleum products is the most important factor in the steady development of the oil processing industry. To lower the content of sulfur, nitrogen, and aromatic hydrocarbons in petroleum fuels the capacities of hydrogenating processes have been stepped up by reconstruction and modernization of existing units for hydrotreating and hydrocracking, on the one hand, and construction of new ones, on the other. At the same time great consideration has been given to developing and bringing into use new catalytic systems of high effectiveness because even small improvements in catalyst characteristics increase the total profitability of the process.

The most widespread industrial catalysts for petroleum distillate hydrotreating are alumina-cobalt-molybdenum and alumina-nickel-molybdenum systems in the form of oxides. Their optimal activity is provided by total sulfiding. Sulfiding insufficiency results in a decrease in the activity and selectivity of the catalyst, reduction of its service life, increase in the initial temperature of the process and therefore reduction of the interregeneration cycle.

There are five industrial processes of sulfiding: using a gas mixture of hydrogen sulfide and hydrogen; a feedstock; a mixture of feed and sulfuring agents; elemental sulfur; preimpregnation with organosulfur compounds (presulfiding) outside the technological plant.

The most well investigated method is sulfiding by hydrogen sulfide. With this sulfiding agent, the catalyst coking is excluded. Long processing in the atmosphere of hydrogen, however, results in overreduction of its active components and decreases its hydrodesulfurization activity. Sulfiding in the gas phase proceeds much more rapidly than in the liquid phase but is accompanied by local overheating due to the low heat capacity of the gas and high exothermicity of the reaction. Local overheating and deficit of hydrogen sulfide may result in catalyst spoiling. Moreover, hydrogen sulfide is remarkable for its high toxicity and pungent unpleasant smell. In industry this method is generally used in the USA.

Sulfiding in the liquid phase by a feedstock is more widespread in Japan, and that by a mixture of a feed and sulfuring agents – in the West and the USA. There is no possibility to achieve total sulfiding by nonrefined oil distillates; in this case the catalyst is coked. The process of sulfiding by a feedstock may be recommended at low temperatures only. It takes a long time to realize this process in industry.

Experience in hydrotreating plants has shown that catalysts sulfided by a feedstock with addition of a sulfuring agent are more active than those sulfided by a feed or a mixture of hydrogen sulfide and hydrogen. In the first case sulfiding is mostly provided by sulfur of a sulfuring agent added at a concentration in a feedstock of 1 wt. %. Cheap organic compounds decomposing at low temperatures have been chosen as sulfuring agents (Table 1).

Carbon disulfide was used for presulfiding before. It is quite dangerous, however, for the environment, so its application is rather limited despite of its high sulfur content. Mercaptans are good sulfuring agents, but their pungent unpleasant smell has forced users to look for other variants. At present dimethylsulfide and dimethyldisulfide are successfully used as sulfuring agents.

Dimethylsulfide, however, is difficult to transport and pipe due to its high volatility, inflammability, and pungent smell. The advantages of dimethyldisulfide are its lower vapor pressure, which reduces its concentration in the atmosphere and decreases the risk of poisoning to personnel, and its lower decomposition temperature and higher flash point (18°C).

Organic polysulfides, specifically di-*tert*-nonylpolysulfide, are effective presulfiding agents, but it is very

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TABLE 1

Sulfuring agent	Content of sulfur, wt.%	Temperature, °C	
		decomposition	presulfiding
Carbon disulfide	84.2	175	240 – 260
Dimethyldisulfide	68.1	200	250
Dimethylsulfide	51.1	250	270
n-Butylmercaptane	34.7	225	260
Di-*tert*-nonylpolysulfide	37.0	160	250

TABLE 2

Index	Hydrotreating at the unit					
	LG-11/ 300-95 JSC Odessa Petroleum Refinery	L-35-11/300 Novopolotsk-nefteorg-sintez	LC-24/7 JSC Ukrtatneft	LK-6u JSC Shimkent-nefteorg-sintez	LK-6u MSE Neftegas	LC-24/5 JSC Moscow Petroleum Refinery
Catalytic system	GO-70 GO-30-7	GO-70 GO-30-7	ACM-M GKD-202p special agent	GO-70 IS-168sh (regenerated)	GP-534 GO-70 GO-117 (regenerated)	GKD-202 GKD-205 GO-70 DT-005N
			Feedstock characteristics			
Density at 20°C, kg/m^3	738	734	836	837	843	849
Content of sulfur, wt. %	0.039	0.019	1.2	0.24	0.91	1.0
Distillation, °C						
IBP	87	83	189	210	204	169
10%	102	100	221	230	228	240
50%	119	120	255	277	277	284
90%	153	156	290	350	360	347
EP	192	179	308	360	368	377
			Product characteristics			
Content of sulfur,						
wt. %	–	–	0.0105	0.01	0.03	0.064
ppm	0.26	0.23	–	–	–	–
			Process parameters			
General pressure, MPa	2.9	2.9	3.2	4.5	4.6	3.1
Temperature, °C	320	330	367	350	355	357
Feedstock space velocity, h^{-1}	5.2	5.0	3.0	4.0	3.4	2.5
Hydrogen-rich gas : feedstock, m^3/m^3	310	330		320	346	230
Hydrogen concentration, vol. %	91.5	89	72	79	86	80

expensive to get sulfur from them [1]. The process of sulfiding by these agents is operatively checked and controlled. To exclude catalyst coking, the process temperature should be less than 340°C.

Many patents of the last 15 years have suggested different ways to presulfide the hydroprocess catalysts outside the catalytic reactor [2 – 10]. Since 1986 more than 30,000 tons of hydrotreating catalysts were successfully used, which had been presulfided outside the technological units according to the Sulficat method of the firm Eurocat.

In accordance with that technology, the catalyst is impregnated by an organic polysulfide compound and kept at higher temperature. The amount of sulfur adsorbed by the catalyst corresponds to the stoichiometric quantity needed to convert the active components into the active form of sulfide. The active metals (molybdenum, cobalt, nickel) in the catalyst sulfided in such a way are in the form of a stable intermediate oxysulfide.

Activation of the presulfided catalyst is realized using hydrogen in a catalytic reactor at 300-350°C. In contrast to the usual way of sulfiding inside the technological unit, this method makes it possible to obtain a catalyst of high activity, speeds up and simplifies bringing a unit into operation and does not require additional amounts of sulfur

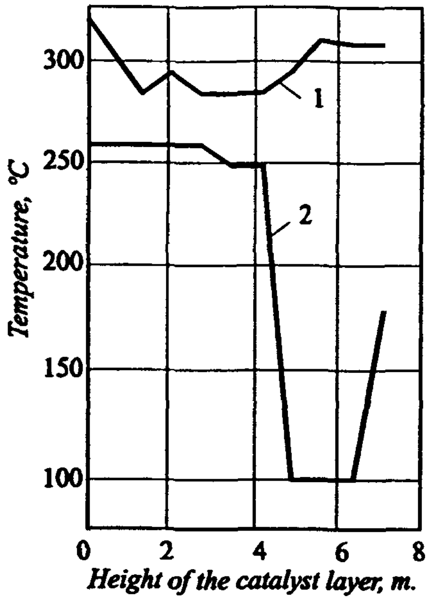

Fig. 1. Temperature profile 4 h after start of sulfiding: 1, 2) in the first and second reactors, respectively.

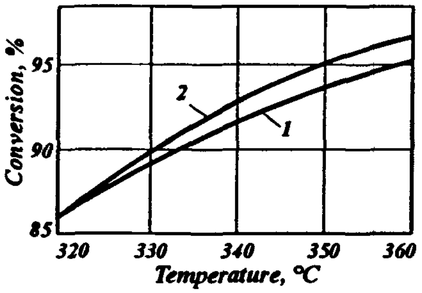

Fig. 2. Influence of temperature on feedstock conversion in hydrosulfuration with the catalyst GO – 70: 1) sulfided by elemental sulfur inside the reactor; 2) presulfided by elemental sulfur outside the reactor.

compounds. The problems of developing and applying the presulfided catalysts have been thoroughly discussed [11 – 16].

The process of sulfiding hydrotreating catalysts by elemental sulfur is widely used at oil processing plants in Russia. There is no disadvantage inherent in sulfiding by hydrogen sulfide or a feedstock with addition of sulfuring agents. The risk of fire and toxicity are lower in this case and this method takes less time and is less expensive. When used under optimal conditions this method makes it possible to achieve 100% sulfiding, which provides high activity and good operational properties of the catalyst [17 – 20].

In industry 15 wt. % elemental sulfur for catalyst sulfiding is charged into the reactor either over the layer or by mixing with the top layer. In this process sulfur occupies some space, which becomes free of the catalyst after sulfiding. This reduces its charge in the reactor and may result in uneven packing of the layer and therefore its non-optimal contact with the feedstock; when a gas-liquid mixture is charged, the liquid feedstock infiltrates through more open channels, creating the least resistance to flow.

The temperature profile of the elemental sulfur sulfiding process is very complex. Figure 1 shows its changes when the package of alumina-nickel-molybdenum and alumina-cobalt-molybdenum catalyst is sulfided at the L-24/7 unit of the Joint Stock Company "Nizhegorodnefteorgsintez".

Industrial catalysts differ one from another not only by the method of production but by the support quality and composition, its texture characteristics, and the content of active components and modifying additives. Thus, when choosing the catalyst (base and auxiliary) package as well as the method of sulfiding, the individual characteristics of the feedstock and hydrotreating units and the requirements of the products are taken into consideration.

The specific characteristics of operating the catalytic systems have been extensively developed and investigated at the Electrogorsk Institute for Petroleum Processing (El INP). Catalytic packages of domestic alumina-nickel-molybdenum and alumina-cobalt-molybdenum catalysts were charged into the reactors for hydrotreating gasoline and diesel distillates at a number of oil processing plants of the former USSR. The results of industrial operation of catalytic systems sulfided by elemental sulfur according to the El INP method are shown in Table 2.

Industrial experience in the operation of catalytic systems sulfided by elemental sulfur has shown their advantages over individual catalysts, with respect to their activity, service life, and reliability, but application of these systems at oil processing units in Russia is limited. As theoretical investigations and long-term pilot tests have shown, this is connected, first of all, with difficulties in controlling the process of sulfiding large amounts of catalyst as well as the lack of technological equivalency between catalytic packages and their composition.

As a result, the problem of developing the method of presulfidation of a hydrotreating catalyst by elemental sulfur outside a catalytic reactor has been set up. This would allow utilizing the operating space of the reactor as much as possible and reducing exothermic effects during activation by hydrogen due to even distribution of sulfur in the catalyst pores, and its preliminary reaction with the active components resulting in the formation of oxysulfides and a drop in the activation temperature.

With the abnormal behavior of the melted sulfur in mind, which can be explained by the change in the molecular structure and mutual conversion of its modifications because of heating, the temperature range of the melted sulfur in contact with the catalyst has been chosen as 120 to 180°C. The catalyst specimen with the calculated amount of sulfur – from stoichiometric up to 70 wt. % in the catalyst – was charged into a flask, deaerated under vacuum, and heated in a nitrogen stream up to the assigned temperature. The flask was constantly rotated for even distribution of sulfur. The contact of the latter with the catalyst should be long enough for its penetration into the catalyst pores. Then it was cooled in a nitrogen stream. This technology is also applicable to regenerated catalysts.

The catalyst sulfided in such a way includes sulfur in quantities greater than stoichiometric. It can be used as a catalyst-activator charged into the reactor as a top layer. Charging the catalyst-activator with the necessary content of sulfur in pores is more promising than its partial unloading after regeneration and replacing it with the fresh one.

Presulfiding the alumina-nickel-molybdenum and alumina-cobalt-molybdenum catalyst by elemental sulfur contributes to a substantial increase in the catalyst strength, which makes it possible to reduce the level of damage during charging of a hydrotreating reactor. Formation of small catalyst particles results in an increase in the pressure differential in the reactor during the process.

To confirm pyrophoricity the presulfided catalyst specimen with 30 % content of sulfur in the pores, which had been cooled down to the ambient temperature, was blasted by air. The temperature in the middle of the layer was checked as a function of time with a thermocouple. It remained constant as long as 1 h.

The results of activity tests have shown that after the activation under conditions equivalent to those in sulfiding by elemental sulfur inside the catalytic reactor according to the previously developed method all catalysts presulfided by elemental sulfur were characterized by a comparable or higher activity in the reactions of hydrodesulfuration. The test results of the industrial alumina-cobalt-molybdenum hydrotreating catalyst GO-70 in the oxide (sample 1) and presulfided (sample 2) form are presented in Figure 2. The concentration of sulfur in the initial catalyst of Sample 2 was 10 wt. %, which was somewhat higher than its stoichiometric amount. Sulfur charging in the case of sulfiding inside the reactor was the same.

The titration conditions were: hydrogen pressure 3 MPa; feedstock space velocity 3 h^{-1}; hydrogen:feedstock 200 m^3/m^3 (normal conditions); temperature 320, 330, 340, 350, 360°C. The feedstock used was a straight diesel cut: density 843 kg/m^3 at 20°C; distillation, °C: IBP 179, 50% 286, 90% 360, EP 367; content of sulfur 1.2 wt. %.

The conditions of presulfiding and subsequent activation depend on the method of production (coprecipitation or impregnation), the texture characteristics of the catalyst, the qualitative and quantitative content of active components in it, as well as the support composition. A catalytic system of high activity can be achieved only if the individual characteristics of catalysts are taken into consideration.

The method of presulfided catalyst production can be easily realized at the existing catalyst plants: either in rotating furnaces or apparatus for support impregnating. Application of the safest sulfuring agent – elemental sulfur – should be regarded as an advantage of the process because this agent is nonvolatile, nonflammable, nontoxic, and, moreover, is neither scarce nor expensive product (most oil processing plants are provided with Claus units for sulfur production; in 1989 its average retail price in the USA was $78.8/ton).

Elemental sulfur easily penetrates the catalyst pores during heating and remains there after cooling. The amount of sulfur incorporated depends on pore volume and content of active metals. The catalyst presulfided in such a way is not pyrophoric and in contrast to most catalysts of similar nature does not require protection from the air.

The advantages of application of such catalyst are as follows: shorter time of activation; high catalytic activity; lower initial temperature of the hydrotreating process; longer interregeneration cycle.

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