Hydrotreating of a Vacuum Gas Oil-Heavy Coker Gas Oil Mixture

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Abstarct—Changes in the chemical composition of the vacuum gas oil in a mixture with heavy coker gas oil in the presence of industrial and laboratory NiMoW/P_2O_5–Al_2O_3 catalyst were studied. The support used was γ-Al_2O_3, prepared from AlOOH powder TH-60 (Sasol), with the following textural characteristics: S_{BET} = 205 m^2/g, V_{pore} = 0.682 cm^3/g, R_{eff} = 48 Å. Alumina was modified with P_2O_5 by incipient wetness impregnation with a solution of phosphoric acid (reagent grade), followed by drying and calcination. The catalysts were prepared by incipient wetness impregnation with a combined solution of Mo, W, and Ni compounds. Before the catalytic test, the catalysts were subjected to sulfidation directly in the hydrotreating reactor of a laboratory setup in a stream of H_2S/H_2 = 70/30 vol %/vol % under 0.11 MPa pressure for 2 h at 500°C. The catalytic properties of the catalysts synthesized were examined under the following conditions: temperature of 360 and 390°C, hydrogen pressure of 5.0 MPa, liquid hourly space velocity of 1.0 h^{-1}, volume ratio of hydrogen to feed of 1000 : 1 nL/L, catalyst loading (0.50–0.25 mm fraction) 27 cm^3. The reactor temperature was controlled accurately to within 1°C, pressure, to within 0.1 MPa, feed rate, to within 0.2 mL/h, and hydrogen flow, to within 0.2 L/h. During the process the contents of sulfur and polycyclic aromatic hydrocarbons, as well as the hydrocarbon-type content and carbon content of the feed and the hydrogenates, were determined. After the tests the catalysts were studied by differential thermal analysis in combination with thermogravimetry (DTA-TGA).

Keywords: vacuum gas oil hydrotreating, heavy coker gas oil, NiMoW/P_2O_5–Al_2O_3 hydrotreating catalysts

The two key challenges currently faced by the petrochemical and oil refining industries are increasing the depth of oil refining and obtaining petroleum products compliant with appropriate normative and technical documents. Meeting these challenges has become increasingly difficult as the quality of feedstocks is deteriorated, with crude oil becoming poorer in quality and heavier and the potential content of light fractions getting lower. In this situation, wider use of destructive oil processing products for increasing the amount of light oil products is an obviously necessary option [1, 2]. Delayed coking is the cheapest and most flexible destructive process [3], which allows significantly increasing the depth of oil refining. Currently, the purpose of delayed coking is changing from coke seen as target product and coker distillates, as byproducts, to coker distillates as target products.

Qualified use of delayed coking distillates presents a problem, especially in view of stringent environmental standards for commercial petroleum products, adopted in the last decade. A combination of delayed coking and hydrotreating processes has received the most widespread use. All coking products are characterized by higher sulfur contents than straight-run fractions, as well as by significant contents of nitrogen, aromatics, and olefins. Refineries tend to involve in hydrotreatment mixtures of gasoline and light coker gas oil with straight-run oil fractions, mainly with the straight-run diesel fraction. Hydrotreating of mixtures of vacuum gas oil (VG) with heavy coker gas oil (HCG) and research thereon are not currently conducted. However, the involvement of HCG in the hydrotreating of VG would increase the depth of oil refining and the yield of light oil

products, essential for treating large volumes of heavy oils.

For VG hydrotreating, a NiMoW/P_2O_5–Al_2O_3 catalyst [4] exhibiting high hydrodesulfurization and hydrogenation activities was proposed. This makes topical studying the changes in the chemical composition of VG in a mixture with HCG during hydrotreating in the presence of NiMoW/P_2O_5–Al_2O_3 hydrotreating catalyst as compared to industrial catalyst.

EXPERIMENTAL

Synthesis of NiMoW/P_2O_5–Al_2O_3 catalyst. The catalyst support, Al_2O_3, was prepared from AlOOH Sasol TH-60 powder. To this end, the AlOOH powder was mixed with water acidified with HNO_3 (pH = 3); the resulting aluminum hydroxide pseudogel was extruded through a spinneret, the extrudates were dried at 60, 80, and110°C for 2 h, further heated at a rate of 1°C/min to 550°C, calcined for 2 h, and then ground to a 0.5–0.25-mm fraction. The resulting support had the following pore structure characteristics: S_{BET} = 205 m^2/g, V_{pore} = 0.682 cm^3/g, R_{eff} =48 Å. Alumina was modified with P_2O_5 by incipient wetness impregnation with a solution of H_3PO_4 (reagent grade), followed by drying and calcination as described above for Al_2O_3.

The NiMoW/P_2O_5–Al_2O_3 catalysts were prepared by incipient wetness impregnation with a combined solution of Mo, W, and Ni compounds: phospho-molybdic acid $H_3PMo_{12}O_{40}·17H_2O$ (reagent grade), phosphotungstic acid $H_3PW_{12}O_{40}·29H_2O$ (reagent grade), nickel carbonate (analytically pure grade), and citric acid (complexing agent). The catalysts prepared were dried for 2 h at 60, 80, and 110°C. For determining the content of the metal oxides and the pore structure characteristics, selected catalysts were calcined at 550°C for 2 h.

Determination of the physicochemical characteristics of the support and the catalysts. The pore structure of the support and the catalysts was determined by low-temperature nitrogen adsorption at 77 K on a Quantachrome Autosorb-1 pore size analyzer. The specific surface area was calculated by the BET method at a relative partial pressure P/P_0 = 0.2. The total pore volume and the pore radius distribution were determined from the adsorption curve using the Barrett–Joyner–Halenda (BJH) model at a relative partial pressure P/P_0 = 0.99.

The Mo, Co, and Ni contents in the catalysts were determined by the X-ray fluorescent method; certified samples were used for calibration. Prior to catalytic testing the catalysts obtained in the oxide form were sulfided for converting the oxides of the active metals to a sulfide form.

The acidity of the pre-calcined oxide catalysts was determined by the temperature-programmed desorption (TPD) of ammonia on a TPDRO 1100 analyzer. The NH_3 adsorption was carried out in a stream of a 1 : 1 (vol/vol) NH_3/N_2 mixture of gases pre-dried on a column packed with NaOH. Within 30 min, full saturation of the sample with ammonia was achieved. In the desorption stage, heating was carried out in a helium stream (30 mL/min) at a rate of 8°C/min. The desorption temperature was in a 25–1000°C range.

Thermal analysis of the catalysts after the tests was carried out on a Netzsch STA 449F3 derivatograph in the temperature range of 30–600°C at a heating rate of 10°C/min in air medium.

Determination of the catalytic activity. Sulfidation of the catalysts was performed directly in a hydrogenation flow reactor in a H_2S/H_2 = 70/30 (vol %/vol %) stream under 0.11 MPa pressure for 2 h at 500°C. The catalytic activity was examined under the following conditions: temperature of 360 and 390°C, hydrogen pressure of 5.0 MPa, LHSV 1.0 h^{-1}, hydrogen to feed ratio of 1000 : 1 nL/L of feed, catalyst loading (0.50–0.25 mm fraction) of 27 cm^3. The reactor temperature was controlled accurately to within 1°C, pressure, to within 0.1 MPa, feed rate, to within 2 mL/h, and hydrogen flow, to within 0.2 L/h.

The catalysts were tested in hydrotreatment of VG and of a VG (90 vol %)+HCG (10 vol %) mixture at a temperature of 360, 390°C, pressure of 5.0 MPa, H_2 : feed ratio of 1000 nL/L of feed, LHSV of 1 h^{-1}. The catalyst particle size was 0.5–0.25 mm, and catalyst loading, 27 cm^3. Table 1 lists the characteristics of the VG and HCG.

Features of the reactions in heterogeneous catalytic processes may be examined only for the reactions proceeding in a kinetic regime. Therefore, it was necessary to determine the reaction regime for the process parameters and hydrodynamic conditions within the reactor chosen. To this end, the Madon-Boudart test was used. This is a method for determining the regime of proceeding of a hetero-geneous process using at least two catalyst samples

with different contents of the active component. In the absence of diffusion hindrance the rate constants of the corresponding, structure-insensitive reactions, normalized to the amount of the active component, should be close, ideally equal [5]. The results of Madon–Boudart test are presented in Table 2.

Table 2 shows that, up to a temperature of 360°C inclusive, there is no diffusion hindrance in the system. To determine the regime for the reactions at up to 420°C temperatures the calculated reaction rate constants were linearized in the coordinates of logarithm of the rate constant of hydrodesulfurization (HDS) ln k_{HDS} vs. $1/T$. The approximation reliability for a linear trend was 0.9897. The lack of inflection points in the plot indicates that the HDS reactions of VG occur in one regime. This is confirmed by the proceeding of the process in kinetic regime throughout the temperature range of interest.

Preliminary experiments revealed no changes in the observed catalytic activity with catalyst particle size decreasing to 0.25–0.075 mm. This confirms proceeding of the process in the kinetic regime on the 0.50–0.25 mm catalyst particles.

Determination of the chemical composition of the vacuum gas oil and the hydrogenates. Hydrogen sulfide was removed from the hydrogenates by 15-min bubbling an inert gas (N_2) at 90° through the sample. Total sulfur content was determined on a Shimadzu EDX800HS X-ray fluorescence analyzer. Quantitative determination of polycyclic aromatic hydrocarbons (PAHs) was carried out on a Shimadzu UV-1700 spectrophotometer; the contents of bicyclic (BAHs) and tricyclic (TAHs) aromatic hydrocarbons were determined separately. The optical densities D of the diesel fuel solution were measured in n-heptane (reagent grade) at characteristic wavelengths of 225, 230, 255, and 375 nm. The content (wt %) of naphtha-

Table 1. Physicochemical characteristics of VC and HCG

Physicochemical characteristics	VG	HCG
Fractional composition		
IBP	342	280
50%	396	
		Cracking distillation
EBP	487	The same
Density, g/cm^3	0.905	0.934
Color, CNT units	2.5–3.0	>8.0
Sulfur content, wt %	2.07	3.02
Iodine value, g I$_2$/100 g	0.9	11.7
Olefins, wt %	1.24	12.8
PAHs, wt %	9.61	10.74

lene (C_n), phenanthrene (C_{ph}), and anthracene (C_a) hydrocarbons was calculated by the procedure from [6].

The hydrocarbon-type content was determined using liquid adsorption chromatography (LAC) on ASK silica gel by the technique developed at Middle Volga Oil Refining Research Institute, Public Joint Stock Company [7]. Hydrocarbons were subdivided into groups based on the refractive index: paraffins-naphthenes ($n_D^{20} < 1.4900$); light ($n_D^{20} = 1.4900$–1.5100), medium ($n_D^{20} = 1.5100$–1.5300), heavy ($n_D^{20} > 1.5300$) aromatics; resins.

RESULTS AND DISCUSSION

For comparative tests, a NiMoW/P$_2$O$_5$–Al$_2$O$_3$ catalyst was synthesized. The support had the pore structure characteristics that were experimentally

Table 2. Madon–Boudart test results

Metal content, wt %	Catalyst	
	Ni$_6$–PMo$_{12}$/γ-Al$_2$O$_3$	Ni$_6$–PMo$_{12}$/γ-Al$_2$O$_3$
Mo	17.20	13.60
Ni	4.70	3.30
Temperature, °C	Rate constants of the HDS reactions, normalized to the number of moles of metals (Mo+Ni) in the catalyst sample, k_{HDSN}/1000, h^{-1} g^{-1} mol^{-1}	
360	1.35	1.44
390	2.34	2.41

Table 3. Characterization of the catalysts used for VG and VG + HCG hydrotreatment

Run no.	Catalyst	NiO			S_{BET}, m²/g		
		NiO	MoO₃	WO₃	S_{sp}, m²/g	V_{pore}, cm³/g	R_{eff}, Å
1	NiMoW/P₂O₅–Al₂O₃	4.8	9.1	14.7	123	0.438	58
2	Industrial	5.0	19.0	–	138	0.482	48

**Table 4.** Results of the comparative tests of NiMoW/P₂O₅–Al₂O₃ and industrial catalyst

Temperature, °C	Feed	Industrial catalyst		NiMoW/P₂O₅–Al₂O₃	
		HDS degree, %	PAH hydrogenation degree, %	HDS rate, %	PAH hydrogenation degree, %
360	VG	92.6	45.7	94.5	51.1
390	VG	98.9	50.0	99.1	54.7
360	VG (90 vol %) + HCG	91.9	42.2	93.6	49.3
390	(10 vol %)	98.8	46.8	98.7	52.6

optimized for vacuum gas oil [8]. The molar ratio Mo/W = 1 providing a maximum HDS activity of NiMoW/Al₂O₃ catalysts was found in HDS experiments with dibenzothiophene, in hydrotreatment of a mixture of diesel fractions and vacuum gas oil [9].

It was previously shown that an increase in the acidity of the hydrotreating catalyst support leads to increased depths of hydrodenitrogenation (HDN) [10, 11], hydrogenation [12–14], and HDS [14, 15] reactions, essential for vacuum gas oil hydrotreating. Along with boron oxide and zeolite additions which increase the acidity of the support, one of the most extensively studied and often proposed modifiers is P₂O₅ used in up to 10 wt % amounts [16–19]. Adding P₂O₅ to the hydrotreating catalyst was shown to lead to
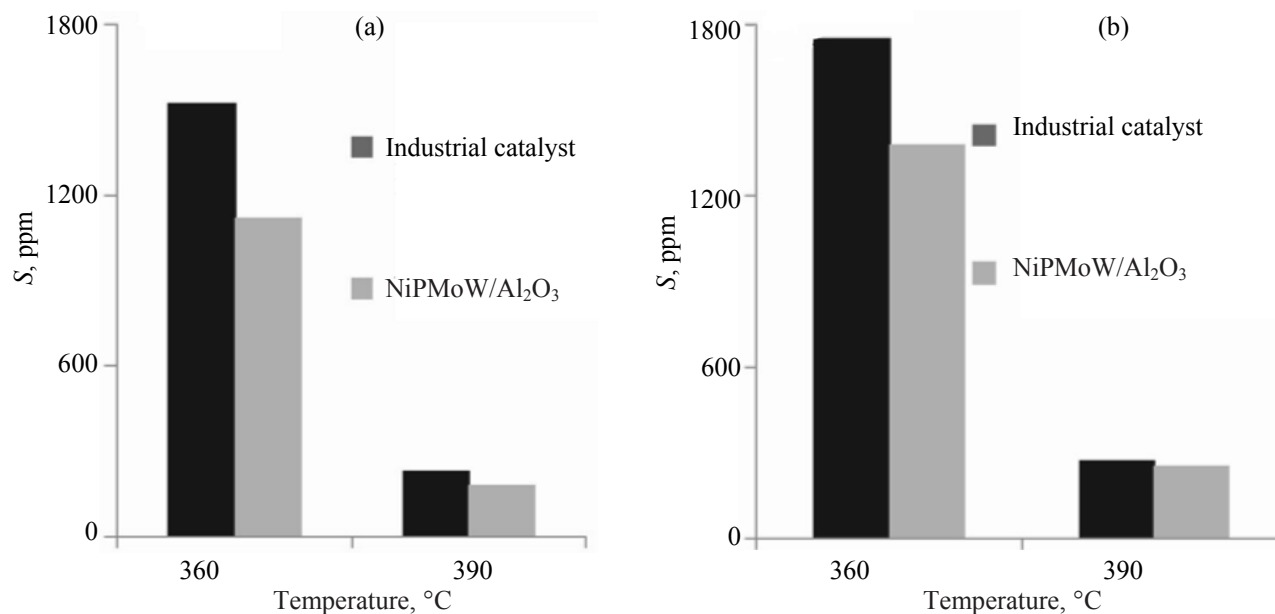
Fig. 1. Sulfur content in the hydrogenates in relation to the temperature and feed: (a) VG and (b) VG + 10 vol % HCG.

Table 5. Hydrocarbon-type content data[a]

Indicator	VG, over indicated catalyst, at indicated temperature					VG+HCG, over indicated catalyst, at indicated temperature				
	feed	no. 1, 360°C	no. 2, 360°C	no. 1, 390°C	no. 2, 390°C	feed	no. 1, 360°C	no. 2, 360°C	no. 1, 390°C	no. 2, 390°C
1. Carbon residue [GOST (State Standard) 19932]	0.09	0.01	0.01	<0.01	0.02	0.14	0.01	0.02	0.02	0.02
2. Hydrocarbons, wt %										
Paraffins-naphthenes	57.50	78.00	79.30	68.10	75.00	53.60	71.30	69.60	68.40	65.10
Light aromatics	9.80	4.50	3.30	6.50	6.90	7.50	6.40	6.70	5.90	13.20
Medium aromatics	4.20	3.20	4.30	9.00	6.80	5.60	8.00	8.40	7.40	3.40
Heavy aromatics	26.60	13.50	12.70	15.90	11.20	30.90	12.70	13.90	17.50	17.40
Resins	1.90	0.80	0.40	0.50	0.10	2.40	1.60	1.40	0.80	0.90

[a] Catalyst no. 1: NiMoW/P_2O_5–Al_2O_3. Catalyst no. 2: industrial.

increased dispersion of MoS_2 particles, thereby favorably affecting its catalytic activity in HDN and hydrogenation reactions [18, 19], as well as to increased catalytic activity in HDS reactions via formation of multilayer MoS_2 stacks [19].

We revealed earlier [4] that 2–5 wt % P_2O_5 additions caused increases in the hydrodesulfurization and hydrogenation rates of the catalyst. Among the NiMo samples, the most active in the hydrotreatment of a mixture of diesel fractions was that with 5 wt %

P_2O_5; the highest HDS activity in the hydrotreatment of vacuum gas oil was demonstrated by the sample with 2 wt % P_2O_5. Therefore, the support for the hydrotreating catalyst in the case of a VG-HCG mixture was modified with 2 wt % P_2O_5. A modern imported industrial catalyst for hydrotreatment of vacuum gas oil served as reference. Table 3 compares the catalysts in terms of the metal content and lists their pore structure parameters: specific surface area S_{BET}, specific pore volume V_{pore}, and effective pore radius R_{eff}.
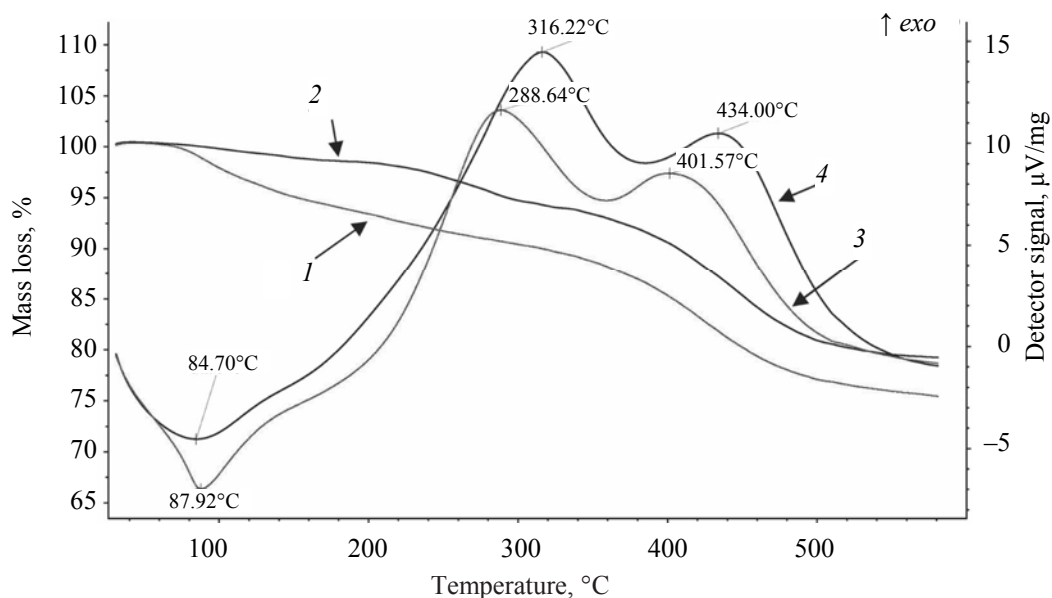
Fig. 2. Thermal analysis data. Mass loss curves: (*1*) industrial catalyst and (*2*) NiMoW/P_2O_5–Al_2O_3. DTA curves: (*3*) industrial catalyst and (*4*) NiMoW/P_2O_5–Al_2O_3.

Table 3 reveals comparable molar amounts of the metals for the synthesized and industrial catalyst samples. With NiMoW/P$_2$O$_5$–Al$_2$O$_3$ containing 2 wt % P$_2$O$_5$, and the industrial catalyst, 5 wt % P$_2$O$_5$ [20], their activities may be compared.

The hydrodesulfurization and hydrogenation activities of the catalysts were estimated by the conversion of sulfur-containing compounds and of PAHs as a percentage of the initial content. Table 4 summarizes the results of the comparative tests. Figure 1 presents data on the residual sulfur contents in the hydrogenates for the VG (a) and VG+10 vol % HCG (b) feeds.

It is seen that the HDS activity, exhibited by the NiMoW/P$_2$O$_5$–Al$_2$O$_3$ catalyst at the two test temperatures for the both feeds, is comparable, though slightly higher, with that of the industrial catalyst. The degree of hydrogenation of PAHs varies with the feed. Specifically, in the case of VG the industrial catalyst exhibits a higher hydrogenation activity, but in the case of the VG+HCG mixture the activity of the laboratory sample is much higher.

Table 5 presents the results of the determination of the hydrocarbon-type content of the feed and the hydrogenates. It is seen that the activity of the laboratory sample is much higher in the case of the VG+HCG mixture.

Figure 2 shows the DTA-TGA data of for the spent catalyst samples.

It is seen that the exothermic oxidation peak of sulfide sulfur for NiMoW/P-Al$_2$O$_3$ occurs at a temperature exceeding that for the industrial catalyst, 316 against 288°C, i.e., sulfide sulfur on the industrial sample is more mobile. The coke contents on the catalysts after the test are nearly identical, 14.71 against 14.59 wt %. The peak of the coke oxidation on the industrial catalyst is also observed at a lower temperature compared to the laboratory sample.

CONCLUSIONS

The NiMoW/P$_2$O$_5$–Al$_2$O$_3$ catalyst proposed allows hydrotreating vacuum gas oil in a mixture with heavy coker gas oil to sulfur contents of <800 ppm at temperatures above 370° C and to those of <200 ppm at 390°C. The NiMoW/P$_2$O$_5$–Al$_2$O$_3$ catalyst sample supersedes the industrial sample in the HDS activity. The proposed and industrial samples exhibit comparable hydrogenation activities in hydrotreatment

of both VG and VG+HCG mixture. The coke contents of the catalysts, that indirectly characterize their stability, are also comparable.

CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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