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PETROCHEMISTRY AND PETROLEUM PROCESSING

Cracking of Vacuum Gas Oil over Poisoned and Passivated Catalysts with Wave-Induced Feedstock Preactivation

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Abstract—The catalytic cracking of heavy oil fractions with wave-induced feedstock preactivation over the catalysts containing passivators of heavy metals provides the same process performance characteristics as over the catalysts, which have not been poisoned with metals.

Keywords: catalytic cracking, passivation, wave treatment, gas oil

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INTRODUCTION

One of the major problems in the refining of heavy feedstocks via catalytic cracking is the fast poisoning of cracking catalysts when heavy feedstocks are used. Thus, the accumulation of metals producing a poisoning effect on a catalyst that is observed when mazut is used as a feedstock.

It is known from the literature data that the most pronounced poisoning effect on fluid catalytic cracking (FCC) catalysts is produced by nickel, which catalyzes dehydrogenation processes at 500°C and thereby decreases the yield of gasoline and increases the formation of coke and hydrogen [1]. Coke and hydrogen are undesirable catalytic cracking products. Coke abruptly decreases the activity of a catalyst and requires its prolonged oxidative regeneration, and the increased formation of molecular hydrogen indicates a growth in the content of aromatics and olefins in cracking products [2–4]. In connection with this, in this work, we have focused our attention on the possibility of reducing the poisoning effect of nickel.

EXPERIMENTAL

Objects and Methods of Study

Passivators and compounds. In this work, different antimony and phosphorus compounds synthetized according to [3] were used as passivators. Antimony(I) trio-(O,O-diisopropyldithiophosphate) was synthesized by the reaction between diisopropyldithiophosphic acid and antimony trichloride. To anhydrous *iso*-propanol (100 mL, 1.31 mol/L) phosphorus pentasulfide (28.4 g, 0.13 mol) was added by portions under intense stirring in an argon atmosphere at 60°C (333 K) and then stirred at 80°C (353 K) for 2 h until the precipitate completely dissolved. To the resulting solution of diisopropyldithiophosphic acid, antimony trichloride (18 g, 0.08 mol) was then added at room temperature, stirred for 1.5 h, and allowed to stand for a night. The solution was separated from the precipitate by decantation and evaporated from excess *iso*-propanol under vacuum. The precipitated light-yellow crystals were washed twice with methanol on a Büchner filter and recrystallized from chloroform. The compound (35.3 g, 58%) with a melting temperature of 71–73°C (344–346 K) was synthesized. In the literature data, the melting temperature is 71–72°C (344–345 K).

Bis-(O,O-diisopropylthiophosphoryl)disulfide was synthesized by the oxidation of sodium diisopropyldithiophosphate with bromine. A solution of diisopropyldithiophosphic acid in excess *iso*-propanol (see section "Antimony(I) trio-(O,O-diisopropyldithiophosphate)") was neutralized with a saturated sodium carbonate solution added drop by drop from a separation funnel to pH 7. Excess *iso*-propanol and water were distilled off under heating in a vacuum, and the residue was dried over phosphorus pentaoxide at 1 mmHg. The yield of sodium diisopropyldithiophosphate was 38.5 g (70% on a phosphorus pentasulfide basis).

The synthesized salt (8.9 g, 0.038 mol) was placed into a three-necked flask, dissolved in anhydrous toluene (500 mL), after which bromine (1.72 g, 0.011 mol) was added with stirring. The reaction mixture was stirred for 3 h until bromine discolored, the precipitate was separated out by filtration, and the filtrate was evaporated in a vacuum. To the resulting oily precipitate, pentane (30 mL) was added, and the yellow trisulfide (B) precipitate was separated by filtration after cooling to –15°C (258 K). The filtrate was cooled to –70°C (203 K), and the disulfide (A) precipitate was separated out by filtration. *Bis*-(O,O-diisopropylthiophosphoryl)disulfide (A) (1.27 g; theor., 21%) was synthesized with a melting temperature of 95–96°C (368–369 K). In the literature data, the melting temperature is 95–96°C (368–369 K).

***Bis*-(O,O-diisopropylphosphoryl)disulfide** was obtained by the method proposed for the synthesis of its neopentyl analogue.

Dry trimethylamine (10.1 g, 0.1 m) was added to a mixture of diisopropylphosphite (16.6 g, 0.1 mol) and sulfur (3.45 g, 0.11 g-atom) in anhydrous benzene (75 mL),. After the exothermic reaction terminated, the mixture was stirred at room temperature for 2 h, and excess sulfur was filtered out. Evaporation was performed in a vacuum. Synthesized salt (C) of trimethylamine and diisopropylthiophosphic acid representing a light-brown oil was used at the second stage without additional purification.

After cooling to 275 K, a solution of sulphonyl chloride (7.8 g, 0.116 m) in benzene was added to a solution of salt C (34.8 g, 0.116 mol) in anhydrous benzene (100 mL) such that its temperature did not increase above 278 K. The precipitate was filtered out, and the residue was evaporated under vacuum until two-thirds of it were removed, after which the settled precipitate was filtered out again. The residue was evaporated in a vacuum and purified by freezing out a benzene solution. *Bis*-(O,O-diisopropylphosphoryl)disulfide (18.5 g, 80%) was synthesized. The structure of the synthesized compound was confirmed by IR, PMR, and mass spectroscopy.

Antimony trichloride was applied in the form of an industrial sample of pure grade.

Triphenylantimony was synthesized by the reaction between antimony trichloride and phenylmagnesium bromide. Antimony trichloride (9 g, 0.04 mol) in anhydrous benzene (200 mL) was added to an ether solution of the Grignard reagent synthesized from magnesium (3.6 g, 0.15 mol) and bromobenzene (25 g, 0.16 mol) at room temperature. The mixture was boiled with stirring for 6 h and decomposed with water, and the organic layer was separated out and dried over calcium chloride. The solution was evaporated under vacuum, and the residue was recrystallized twice from ethanol. Triphenylantimony 99.5 g, 68%) with a melting temperature of 52°C (325 K) was synthesized. In the literature data, the melting temperature was 52°C (325 K).

Triphenylphosphine was applied as an industrial product of chemically pure grade.

Antimony(III) oxide is an industrial reagent of chemically pure for analysis grade or a technical product of the Ministry of Nonferrous Metallurgy.

Vacuum gas oil subjected to cracking was obtained from distilling a mixture of West Siberian and Tatar oils and boiled in the range of 573–732 K; it contained 1.6 wt % of tars and 1.5 wt % of sulfur and the density was 0.908 g/cm^3.

To deposit nickel onto DA-250, a fresh catalyst portion was impregnated with a nickel acetate tetrahydrate solution and dried in air for 10 h and then at 160°C for 4 h. The sample was calcinated in air at 600°C for 3 h. The finished sample containing 0.5 wt % nickel was synthesized in this way. A passivator (antimony) was deposited onto the poisoned catalyst by impregnating the latter with a benzene solution of $[(i\text{-}C_3H_7O)_2PS_2]_3Sb$ and allowing it to stand for a night, after which the catalyst was dried and calcinated in air under the same conditions as after the deposition of the heavy metal. The resulting sample contained 0.5 wt % of antimony.

The wave treatment and catalytic cracking of feedstocks were performed according to the methods described in [5].

Analysis of the Composition of Cracking Products

A quantitative analysis of the gasoline and diesel fractions was performed on a Crystal-Lux 4000M gas-liquid chromatograph with a flame ionization detector, a Supelco Petrocol capillary column of 0.25 mm × 50 m in size using helium as a carrier gas in a temperature-programmed regime.

A qualitative analysis of the gasoline fraction was performed by chromatographic mass spectrometry on a Finnigan MAT 95 XL instrument equipped with a chromatograph incorporating a capillary column (0.25 mm × 30 m) with the SE-30 stationary phase using helium as a carrier gas (1.5 cm^3/min). The analysis was performed in the following temperature-programmed regime: heating from 30 to 120°C at a rate of 5°C/min and further heating at a rate of 10°C/min to 270°C with exposure at this temperature for 10 min. Mass spectra were recorded in an electron impact regime at an ionization energy of 70 eV. Reaction products were identified by comparing their mass spectra with the spectra of compounds contained in the software library. The fractional and group compositions of the synthesized fractions were determined according to the ASTM methods [6].

Determining the Characteristics of Diesel Fractions

The diesel fraction obtained as a result of cracking were stabilized to remove light-boiling components and to determine the yield of the target fraction. To accomplish this, after hydroforming, the product was placed into a Claisen flask equipped with a reflux condenser with a length of 20 cm, a direct cooler, a prolong, and a receiving tank. The flask was slowly heated and used to collect 1–1.5-g fractions. After each light fraction was stripped out, the closed-cup flash point of

Table 1. Effect of nickel poisoning and passivation on the yield of major products* in the catalytic cracking of vacuum gas oil on the RSG-61D catalyst

Parameter	Catalyst		
	RGS-61D	RGS-61D + 0.65 wt % of Ni	RGS-61D + 0.65 wt % of Ni + 0.48 wt % of Sb
Yield, wt %:			
gasoline	42.7	30.8	40.4
fraction 200–300°C	22.1	21.0	19.1
coke	6.6	9.4	7.3
gas**, cm^3/g, including	5.9	5.8	5.7
hydrogen	22.9	103.0	45.0
methane	4.2	4.4	5.1
ethylene	2.4	2.1	2.5
ethane	1.6	1.3	1.8
propylene	9.8	7.5	
propane	1.3	1.1	
C_4 hydrocarbons	10.8	9.9	

* All of the cracking parameters given in the tables and the figures are arithmetic means for the values obtained in four to five independent experiments. In turn, the yields of cracking products were analyzed three to four times in each experiment (except the yield of coke). The deviation from mean did not usually exceed 0.3 wt % for the yield of gasoline, 0.4 wt % for the yield of the fraction 200–300°C, 3 rel % for the yield of hydrogen, and 3–7 rel % from a determined value for the yield of other gases.

** The yields of gases in this work are given in cm^3 (under normal conditions) per gram of passed feedstock.

a bottom residue was determined. Each stripped fraction and bottom residue were also analyzed by gas-liquid chromatography.

RESULTS AND DISCUSSION

The described method provides the best way to model the processes occurring in industry during the deposition of nickel onto catalysts. The effect of nickel on the results of vacuum gas oil cracking was studied using the industrial RSG-6Ts catalyst as an example. The obtained data were compared with the results obtained on a nickel-free catalyst sample (Table 1).

As can be seen from the data of Table 1, the yield of gasoline in vacuum gas oil cracking at 500°C is 11.9 wt % lower and amounts only 30.8 wt %, and the yield of hydrogen grows by nearly 4 times, when nickel is deposited to a level of 0.65 wt % on a nickel basis (the mentioned level of nickel can really be attained in refining a metal-containing feedstock on industrial plants) compared with the fresh catalyst at the same temperature. The total yields of hydrocarbon gases for the aforementioned samples are 4.9 and 5.8 wt %, respectively.

According to the literature data [2], the best results on the reactivation of nickel-poisoned catalysts at 500°C can be attained using antimony-containing compounds as passivators at a mass ratio nickel : passivator (based on Sb) of 1 : 1 + 1.5 : 1. Here and below, in this work, *tris*-(O,O-diisopropyldithiophosphate)antimony, which has gained the widest recognition at industrial catalytic cracking plants, was used to passivate nickel, if not otherwise specified. Moreover, this passivator works well in the reactivation of faujasite-containing catalysts used in this study at FCC temperatures on laboratory plants. As can be seen from a comparison of the data from Table 1, the treatment of the poisoned catalyst with the passivator in the amount of 0.48 wt % based on antimony in the cracking of vacuum gas oil at 500°C results in a high degree of catalyst reactivation; the gasoline yield increases by 9.6 wt %, the hydrogen yield decreases twofold, and the formation of coke is reduced by 22 rel %. The obtained results agree with the literature data on the passivation of nickel on cracking catalysts with *tris*-(O,O-diisopropyldithiophosphate)antimony [2].

Hence, the reactivation of the RSG-6Ta nickel-poisoned high-alumina catalyst at a cracking temperature of 500°C leads to an increase in the gasoline yield and the total yield of gaseous olefins. The passivation of nickel provides a decrease in the yield of hydrogen and coke. In other words, the application of an antimony-containing passivator considerably reduces the poisoning effect of nickel.

The established regularities of change in the yields of cracking products due to the application of an antimony containing passivator at 500°C were verified on the DA-250 faujasite-containing catalyst, which have a twofold smaller amount of rare-earth elements and a different composition of their matrices. Hydrotreated vacuum gas oil (HVG) was used as a cracking feedstock.

Table 2. Effect of nickel poisoning and passivation on the yield of major products in the catalytic cracking of vacuum gas oil on the DA-250 catalyst (on a 68% conversion basis)

Parameter	Catalyst	
	DA-250 + 0.4 wt % of Ni	DA-250 + 0.4 wt % of Ni + 0.4 wt % of Sb
Yield, wt %:		
gasoline	29.3	31.1
fraction 200–300°C	17.1	23.4
coke	4.8	3.5
gas, cm^3/g, including	4.3	3.1
hydrogen	50.4	35.1
methane	2.5	2.2
ethylene	1.9	1.4
ethane	0.8	0.5
propylene	5.8	5.2
propane	1.1	0.6
C_4 hydrocarbons	6.0	3.7

As can be seen from the data of Table 2, the use of an antimony-containing passivator on the DA-250 catalyst in the cracking of HVG-1 increases the total yield of light products (gasoline and fraction 200–300°C) and decreases the formation of coke and the yield of hydrogen on the poisoned nickel sample as in the case of the RGS-6Ta catalyst.

The deposition of nickel leads to the appearance of a great amount of strong acidic sites and, thereby, to an abrupt decrease in the yield of the gasoline fraction in comparison with the fresh catalyst sample and an increase in the yield of coke and hydrogen at 500°C. The use of a passivator partially suppresses strong acidic sites, which leads to an increase in the yield of gasoline and a decrease in the formation of coke, hydrogen, and hydrocarbon gases at 500°C.

Some data on the dependence of change in the gasoline and hydrogen yields on the DC-250 catalyst with an amount of deposited nickel of 0.4% and an antimony-based passivator were obtained at 500°C (Fig. 1). As can be seen, a decrease in yield is up to 5.5 rel %, and the hydrogen yield is reduced to 60%.

Similar effects were observed when using the foreign ROC-1 and Reduxion LS-60P catalysts. Taking into account the orientation of these catalysts to a higher cracking temperature, the studies were performed at a temperature of 560°C. The obtained data are given in Table 3.

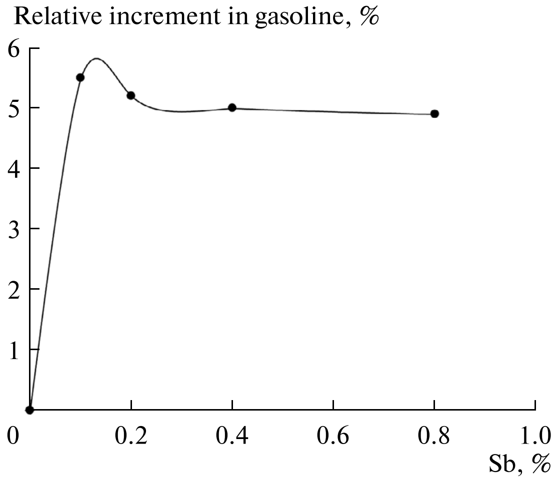

Fig. 1. Curve of change in the gasoline yield for the use of an antimony-based passivator.

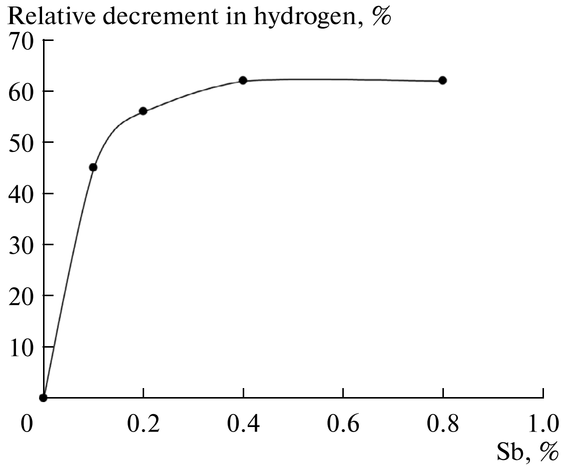

Fig. 2. Effect of the passivator content on the hydrogen yield.

Table 3. Cracking and passivation data for the ROC-1 and Reduxion LS-60P catalysts. Hourly space velocity, 30 h^{-1}*

Products	ROC-1			Reduxion LS-60P		
	0.40% Ni	0.40% Ni + 0.40% Sb*	Δ rel.	0.42% Ni	0.42% Ni + 0.35% Sb**	Δ rel.
Benzene	33.5	35.2	+5.1	28.6	30.3	+5.9
Fraction 200–300°C	18.1	20.1	+11.0	18.8	19.4	+3.1
Coke	7.5	5.2	–26	7.4	6.6	–10.8
Gaseous products including	12.7	10.1	–21	24.5	24.6	+0.5
H_2	0.91	0.77	–18	1.42	1.19	+16
C_2H_4	0.6	0.3	–	2.0	2.0	–
C_3H_6	3.2	3.2	–	6.3	6.8	–
C_4H_8	2.9	1.9	–	6.8	6.9	–

* Here and in the following tables, data from 2–3 parallel experiments are given.

** Passivator is *tris*-(O,O-diisopropylphosphorusdithiolate).

Table 4. Characteristics of the fuel fractions separated from the cracking products

Characteristic	DA -250	DA-250 + 0.4 wt % of Ni	DA-250 + 0.4 wt % of Ni + 0.4 wt % of Sb
Gasoline composition			
Paraffins	24	22	22
Olefins	32	12	22
Naphthenes	7	7	7
Aromatics	37	59	49
RON	94	98	96
Cetane number of the diesel fraction	28	21	24
Diesel fraction density, kg/m^3	0.821	0.852	0.838
Sulfur content in the diesel fraction, %	0.2	0.14	0.14
Freezing point of the diesel fraction, °C	–17	–19	–16
Flash point of the diesel fraction, °C	65	62	65

As can be seen, a considerable increase in the yield of gasoline and a decrease in the yields of hydrogen and coke were also observed in this case with a passivator. The diesel fraction yield was also observed to restore on the first catalyst.

Hence, some common trends of change in the yield of cracking products are observed on the traditional cracking catalysts due to the passivation of the poisoning effect of nickel, and the results attained by the application of passivators are as follows:

(a) the change in the amount of coke after passivation from 10 to 25 rel %;

(b) the change in the yield of gasoline after passivation from 5 to 25 rel %;

(c) an increase in the yield of coke from 10 to 25 rel % depending on a catalyst.

Then, we synthesized some cracking product samples on an enlarged plant under similar conditions on the three DA-250 samples, namely, the initial, nickel-poisoned, and passivated catalysts, to determine the principal characteristics of fuels according to the test procedure.

The gas-liquid chromatography data on the composition of gasoline, its characteristics, and the characteristics of diesel and boiler fuels are given in Table 4. As can be seen, poisoning with nickel leads to an increase in the content of aromatics and the octane number and a decrease in the olefin content. At the same time, the cetane number considerably decreases, and the density of the reaction products grows.

Then, we performed comparative studies on the cracking of activated and nonactivated feedstocks in the presence of nickel and passivators under identical conditions. Feedstock 2 was used in all cases, and the obtained data are given in Tables 5 and 6.

As can be seen, the activation effect also persists on the nickel-poisoned catalyst, when the activity abruptly decreases compared with the traditional system. This allows us to state that the activation effect persists, even for a heavy feedstock, which results in

Table 5. Cracking of non-hydrotreated vacuum gas oil on the DA-250 catalyst containing 0.5 wt % of nickel

Products	420°C		500°C	
	immediately after activation	initial feedstock	immediately after activation	initial feedstock
Gasoline fraction $<C_{11}$	44	32	52	38
Diesel fraction C_{11}–C_{16}	27	26	14	17
Gas + coke	15	25	10	20

Table 6. Cracking of non-hydrotreated vacuum gas oil on the DA-250 catalyst containing 0.5 wt % of nickel and 0.5 wt % of antimony

Products	420°C		500°C	
	immediately after activation	initial feedstock	immediately after activation	initial feedstock
Gasoline fraction $<C_{11}$	37	33	56	42
Diesel fraction C_{11}–C_{16}	19	18	24	24
Gas + coke	18	18	13	16

Table 7. Cracking of a mazut-containing feedstock on the nickel-poisoned DA-250 catalyst (0.5% of Ni) before and after passivation (0.5% of Sb) at 500°C. Feedstock 1 + 10% of mazut

Products	DA-250 (0.5% Ni)		DA-250 (0.5% Ni + 0.5% Sb)	
	immediately after activation	initial feedstock	immediately after activation	initial feedstock
Gasoline fraction $<C_{11}$	40	32	41	34
Diesel fraction C_{11}–C_{16}	16	16	21	18
Gas + coke	5	22	17	19

the deposition of nickel on the catalyst in the amount of 5000 ppm.

In this case, the use of an antimony-based passivator also provides a considerable increase in the yield of gasoline, a slight decrease the yield of coke, and a 70% decrease in the yield of hydrogen.

To model the refining of heavy feedstocks, we have further studied the conversion of a mazut-containing feedstock. The data are given in Table 7. As can be seen, the effect of activation on the yields of the target products persists in this case despite a much slighter effect of the passivator.

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