

RADIOISOTOPE STUDY INTO Co AND Ni CONTAINING CATALYSTS FOR PETROLEUM RESIDUA HYDROTREATING

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A comparative radioisotope study into alumina- and silica supported Co, Ni and Co+Ni catalysts has been carried out. Catalysts were characterized by physical and chemical methods and tested during hydrotreating (HTR) of oil residua of West-Siberian petroleum. Some dependencies among catalyst composition, carrier support, the number, type and productivity of active sites, and catalyst functioning under oil residua HTR have been found. The study has permitted us to put forward some criteria to evaluate the results of radioisotope testing with the aim of designing a catalyst composition optimum for a definite refining process. Some cheap catalysts-adsorbents for preliminary treating of heavy crudes, before they are applied to the main oil refining processes have been designed.

1. INTRODUCTION

Involving heavy residual oils into refining processing makes it of major importance to have effective catalysts for oil HTR. Some major concepts of HTR reactions and architecture of the supported catalysts have been already formulated [1 - 22]. Nevertheless, studies into supported catalyst composition and principles of their functioning are still very urgent to which fact testifies a great number of articles and reviews [10, 11, 23 - 29] which are mainly focused on the issue of catalyst composition and not so often on reaction mechanisms. Radioisotope technique offers us extra opportunities to obtain unique information on active sites number and their functioning and heterocompound transformation mechanisms. [30 - 36].

In this paper the comparison of the results of catalyst radioisotope testing during model reaction of thiophene HDS with the data of residual oil HTR on the same catalysts is being undertaken. It aims at adequate evaluating of both methods potentials to design the best catalyst composition for an actual HTR process.

2. EXPERIMENTAL

2.1. Catalyst preparation, characterization and pretreatment

More than 70 Ni- and Co-containing catalysts were synthesized and studied. Catalyst samples were prepared by wet impregnation of γ -Al₂O₃ (specific surface - 212 m²/g, pore volume - 0.8 cm³/g, pore average D - 124 Å) and of SiO₂ (specific surface - 363 m²/g, pore volume - 0.96 cm³/g, pore average D - 98 Å). Impregnation procedure was carried out (i) using water solutions of Ni or Co nitrates for preparing Ni or Co catalysts, or (ii) using joint solution of Co and Ni nitrates - for Ni+Co catalyst samples preparing. After impregnation the catalysts were air dried for 24 h at room temperature and 2 h at 110°C. Metal surface amount in the samples varied in the range of 1 - 25 %.

All the carriers and catalysts were studied by physico-chemical methods. Pore structure was determined by Hg porosimetry technique using *Cultronix* automatic porosimeter. Metal reduction degree was determined by volumetric technique. Metal concentration in the catalysts was measured by atomic absorption technique.

Two forms of the catalysts were used - reduced and sulfidized. Sample reduction was carried out in the flow of purified H₂ for 10 h at 400°C. Sulfidation of preliminary reduced catalysts was made by elemental sulfur in hydrogen atmosphere (3 MPa, 380°C, 1 h).

2.2. Residual oil hydrotreating technique and product characterization

Residual oils of West-Siberian petroleum contained: asphaltenes - 4.3 % wt, sulfur - 2.3 % wt, V - 40 g/t, Ni - 60 g/t. Residual oil HTR was carried out in a 250 cm³ stainless steel autoclave (5 MPa H₂ pressure, 380°C, 5 h). Sulfur amount in crudes was determined analytically. Derivatographic measurements of coke deposits on the catalyst were made.

2.3. The technique of HDS experiments with radiochromatographic analysis of the products.

2.3.1. *Catalyst sulfidation* was carried out in a pulse microcatalytic installation. The microreactor in the form of U-tube made of pyrex was loaded with 100 mg of the catalyst and linked with the gas-liquid (GL) chromatograph. The rest of the reactor volume was filled with quartz. All catalysts were preliminary subjected to He flow at 200°C for 2 h, then by H₂ flow, 400°C, 4 h. After that they were sulfidized. As sulfidizing agent either 5 % H₂S/H₂, in which H₂S was labeled by ³⁵S isotope,

or thiophene- ^{35}S was used. $\text{H}_2\text{S}/\text{H}_2$ sulfidation lasted for 1 h at 450°C . Further on the catalyst was again treated by He at the same temperature for 30 min. to get rid of adsorbed H_2S .

Sulfidation by thiophene- ^{35}S was made by 3 μl thiophene pulsing into the reactor at 360°C with further chromatographic analysis of the products. After H_2S curve became constant thiophene- ^{35}S pulsing was stopped. After sample sulfidation was over, reactor temperature stabilized at 360°C . Then the catalyst either was taken out of the reactor for sulfide sulfur amount measurement or was tested in the reaction of thiophene HDS.

2.3.2. The technique of HDS experiments with radiochromatographic analysis of the products and mathematical treatment of experiment results. After sulfidation procedure catalyst samples labeled by ^{35}S were tested in the thiophene HDS reaction. Unlabeled thiophene was injected into the reactor by pulses, 1 μl each. To measure reaction product radioactivity a flow proportional counter installed in the outlet of the chromatograph was used. Based on the results obtained some curves of H_2S molar radioactivity (MR) dependencies on H_2S amount (cm^3) are built equivalent to the dependencies on reacted thiophene amounts. Mathematical treatment of the experimental curves allows us to approximate the dependencies we obtained by exponential equations and to calculate the amount of mobile sulfur on each type of active site and productivities of these sites [35].

3. RESULTS AND DISCUSSION

3.1. Radioisotope testing

Preliminary experiments with various amounts of active metal on the catalyst have shown that catalytic activity curves of the samples under study pass through a maximum, depending on an active component amount. The maximum area for all the contacts under study is in the range of 7.0 - 7.6 %. So, those catalyst samples that contain the given amount of active metal have been studied in detail. The results are shown in Tables 1 and 2.

Measurements of radioactivity of thiophene hydrogenolysis products on all the catalysts containing sulfide sulfur labeled by ^{35}S show that radioactivity is present only in H_2S formed. Thiophene that leaves the reactor does not contain radioactivity, which points to the absence of isotope exchange between thiophene sulfur and catalyst sulfide sulfur. In the intervals of thiophene pulses into the reactor or under special experiments any noticeable amount of H_2S formed is not found, i.e. any marked sulfidized catalyst reduction does not occur. H_2S is formed only as a product of thiophene hydrogenolysis.

Table 2 gives equations for the curves of dependencies of H_2S molar radioactivity (MR) on the amount of H_2S formed under thiophene HDS on the catalysts sulfidized by radioactive sulfur. One can see that these equations are monoexponential, i.e. Co or Ni catalysts or Co+Ni catalysts have one type of H_2S formation site while Co(Ni) promoted Mo catalysts have two types of sites differing on the mobility of sulfur, i.e. productivity [35].

Figure 1 shows that treating the reduced catalyst by $\text{H}_2\text{S}/\text{H}_2$ always results in much deeper sulfidation as compared to thiophene. Share of mobile sulfur in samples sulfidized by $\text{H}_2\text{S}/\text{H}_2$ ranges within 11 - 50 % and in Ni or Co+Ni catalysts it is higher than in Co ones. It is true both for alumina- and silica supported catalysts and may be due either to high dispersion of Ni-sulfide particles as compared to Co-sulfide ones or to probable CoS_2 phase formation. It is also essential that on alumina supported catalysts, sulfidized by $\text{H}_2\text{S}/\text{H}_2$, mobile sulfur share is larger than on analogous catalysts supported on silica. It might also be accounted for by higher dispersion of sulfide particles supported on alumina as compared to that of particles supported on silica.

Unlike in catalysts sulfidized by $\text{H}_2\text{S}/\text{H}_2$, in catalysts sulfidized by thiophene sulfidation does not reach maximum possible values and all sulfide sulfur formed under sulfidation by thiophene is mobile. Major portion of mobile sulfur is on Co/SiO₂ sulfidized by thiophene (sample 2a in Table 1) - 2.42 % and the least (0.63 %) - on the same catalyst sulfidized by $\text{H}_2\text{S}/\text{H}_2$ (2b). In the first case mobile sulfur equals 100 % of all catalyst sulfide sulfur and in the second - only 11 %. Productivity of Co/SiO₂ catalyst active sites is also much dependent on a sulfidation procedure - under $\text{H}_2\text{S}/\text{H}_2$ sulfidation it is twice as high as under thiophene. It can be also noted here that this difference is common to other catalysts. In some cases it is noticeably large while in others not (for instance, for Ni/SiO₂ it is not higher than 10 %). We may suppose that under full sulfidation the formation of a substantial amount of immobile sulfur encourages active site formation that have more mobile SH groups as compared to a phase where all sulfur is mobile. If compare Co/SiO₂ and Co/Al₂O₃ catalysts, sulfidized in the same way, one can see that productivities (P) of active sites of these are close. It can be caused by an insignificant effect of carrier nature on reactivity of active sites and by an essential effect of a carrier on the number of the sites.

An effect of active phase metal nature on catalyst active site productivity is clearly seen in the sequence Co - (Co+Ni) - Ni. In all the catalysts supported by one and the same carrier and sulfidized in the same way the productivity grows in the sequence $\text{Co} \leq (\text{Co}+\text{Ni}) \leq \text{Ni}$. Thus, SH groups of Ni-sulfide particles demonstrate higher reactivity in H_2S formation under thiophene HDS conditions than analogous SH groups connected with Co. A possible explanation of these dependencies might be searched within Bond Energy Model, recently developed by Topsøe *et al* [37].

The results of radioisotope testing permit us to single out three catalysts with the best characteristics - Co/SiO₂ (sample 2a), (Co+Ni)/Al₂O₃ (5b) and Ni/Al₂O₃ (3b). Sample 2a is characterized by the highest amount of mobile sulfur, though its active site productivity is the lowest and it demonstrates no high activity in thiophene HDS. Sample 5b demonstrates the highest thiophene conversion, its mobile sulfur amount is actually the same as in sample 2a, and *P* is considerably higher than in most of catalysts under study. Finally, sample 3b has the highest *P*, highest thiophene conversion and relatively small amount of mobile sulfur. To evaluate the effect of the given parameters on the catalyst functioning under real conditions we have compared them with the data obtained in the course of hydroconversion of residual oil.

3.2. Hydrotreating of residual oil

In the course of the experiments it has been found that, the same as in the above described experiments, most effective have proved catalysts containing 7.5 % metal. Catalysts with 3.4 % metal loading were ineffective. Catalytic activity of samples with metal loading 10 % and higher did not exceed that of the catalysts with 7.5 % metal content.

The data about hydrotreating of residual oil is given in Table 3. First it should be stressed that all the catalysts show a rather high degree of selectivity towards residual oil containing metals (Ni, V) that are poisons for cracking catalysts. The catalysts demonstrate different degree of activity towards the desulfurization reaction, depending on the nature of an active metal and support (Fig. 2). The most active is Co/SiO₂ in reduced form (sample 2a, Table 3) - residua desulfurization degree is 55.7 %. Somewhat less active are reduced catalysts Co/Al₂O₃ (1a) and (Co+Ni)/SiO₂ (6a) - 26 % and 27 % correspondingly. Ni reduced catalysts on alumina (3a) and silica (4a) show much less desulfurization activity - 18.0 % and 16.5 % correspondingly. Reduced Co/SiO₂ shows the highest activity in relation to deasphaltization and the lowest towards coke formation. In this catalyst on the silica surface metallic Co of fine dispersion with crystallite size 25 Å has been found. No formation of surface compounds with support is observed. The catalyst has a high specific surface 307 m²/g pore volume 0.78 cm³/g, pore average D 46 Å. Co reduction degree is 97 %. If compare pore structure of the support and catalyst one can see that Co loading does not much change the value of specific surface and pore size. It is possible that in the course of the reaction with sulfur containing crudes Co-sulfide particles formation takes place and they are active in hydrogenation (HYD) reactions. Catalyzing residua asphaltenes HYD they practically completely adsorb metals (Ni and V), which leads to a high degree of residua demetallization. Co sulfides as well as pure Co on silica do not catalyze HYD process of hydrocarbons, which is proved by a low coke deposition on these catalysts.

Co/Al₂O₃ in its reduced form (1a) has a sharp difference from Co/SiO₂: desulfurization degree is twice as low and asphaltene disintegration degree is about 50 %. Demetallization degree is lower too. In all probability, incorporation of some part of Co particles in the Al₂O₃ carrier material decreases the ability of Co/Al₂O₃ to interact with the sulfur of residua heterocompounds.

Ni/SiO₂ reduced catalyst (4a) differs with Co one on its catalytic action. Its desulfurization degree is more than three times lower but it is active in asphaltene HYD, demetallization and coke formation. These data testifies to the fact that metallic Ni on silica weakly interacts with the sulfur of sulfurorganic compounds from residual oil and more actively in HYD and deHYD reactions. Reduced Ni/Al₂O₃ (3a) is more active than Ni/SiO₂ in reactions of C-C bond break and coke formation and less active in asphaltene HYD.

Sulfidized forms of Co and Ni catalysts are essentially different from reduced forms of this catalysts on their catalytic activity, which supposes other nature of their interaction with oil residua components. All the sulfide catalysts have proved to be less active in deasphaltization but more active in coke formation (Tab. 3, Fig. 3). Sulfidized Co/SiO₂ (2b) shows the least degree of desulfurization - 13.6 % and highest degree of demetallization among the sulfide catalysts. Obviously, Co sulfide particles in 2a are not so active in desulfurization than reduced Co particles of sample 2b. Sulfidized Ni/Al₂O₃ catalyst (3b) shows rather low activity in oil residua desulfurization, the same as in demetallization and tends to coke formation. A high activity in oil residua desulfurization has been shown by sulfidized (Co+Ni)/Al₂O₃ catalyst (5b) - 46 % and at the same time its degree of demetallization is the lowest - 61 %. Its coke deposition is 4.6 %.

3.3. Comparative study of radioisotope testing and residual oil hydrotreating data

While comparing the data of radioisotope testing with the results of residual oil HTR one can see a correlation between residual oil desulfurization degree and the amount of mobile sulfur on the catalyst (Fig. 4). Previously we observed a linear dependency between thiophene conversion and the amount of mobile sulfur in CoMo catalysts [33, 34]. However, as it was found later [35], this dependency was true not in all cases but only for the catalysts active sites of which are characterized by close values of productivity. In Table 1 one can see no correlation between thiophene conversion and the amount of mobile sulfur due to the fact that active site *P*s of these catalysts differ from each other as much as two - threefold. In case of residual oil, however, such correlation is seen. One can suppose that a large number of contained in crudes and subjected to desulfurization sulfurorganic compounds which possess different degrees of stability in destruction processes as if levels the

values of P of different catalysts.

Hence, it seems we could conclude that such value as productivity is not essential when we deal with processes based on real crudes. But actually it not so at all. It was rather surprising to establish another linear dependency - between productivity of H_2S formation active sites and coke formation on the catalyst - a secondary process in relation to HDS and H_2S formation (Fig. 5). To some extent this dependency can be explained by carrier acidity on coke formation and hydrodesulfurization. The interdependency between carrier acidity and coke formation is commonly known and the dependency between catalytic activity and carrier acidity is marked by Welters *et al.* [38, 39]. Tables 1 and 3 show that the samples of analogous composition and sulfidized in the same way but supported on different carriers differ on the amount of coke deposition and site productivity - for Al_2O_3 -supported catalysts these values are higher than for their SiO_2 -supported analogs. But this fact can only partially serve as an explanation to the marked dependency. For instance, by acidity one cannot explain higher tendency of Ni-containing catalysts towards coke formation. It seems probable that the higher site productivity the more hydrocarbon fragments are formed in the course of destruction of sulfurorganic molecules and the higher coke formation is.

This supposition is confirmed when we compare the results of residual oil HTR on the above described catalysts non-containing Mo with the results of the same procedure on the commercial Ni-Mo/ Al_2O_3 sulfidized catalyst (see Table 3, sample 7). This catalyst has a high desulfurization ability, being inferior only to catalysts 2a and 5b, but it displays rather low demetallization activity and the strongest tendency towards coke formation. The results of radioisotope testing of Ni-Mo/ Al_2O_3 were submitted and discussed in [35]. In this paper we present radioisotope testing data only for one, mentioned above, commercial catalyst (the last lines of Tables 1 and 2, sample 7) for comparison with data obtained for non-containing Mo catalysts. Sample 7 is characterized by the presence of two types of active sites, "rapid" and "slow", P_s of which are 20.1×10^{-2} and 5×10^{-2} correspondingly and the number of the "rapid" sites is 25 % of the total number of the both types of the sites. The amount of mobile sulfur is 41 % of the total sulfide sulfur in catalyst 7. On this catalyst under the same experimental conditions as for the other catalysts thiophene HDS conversion is 59 % *i.e.* much higher than on the catalysts without Mo.

We believe that on the Mo catalyst promoted by Ni or Co the "rapid" sites are related to Mo and the "slow" ones - to Ni or Co. It was shown [33 - 35] that the unpromoted Mo/ Al_2O_3 catalyst has one type of the sites of low P ($\approx 5 \times 10^{-2}$), low catalytic activity in the thiophene HDS (conversion = 12 %) and the share of mobile sulfur is about 20 % of the total sulfur amount on the catalyst. Introducing promoter (Ni or Co) increases P of active sites related to Mo, though some part of these are blocked by Ni(Co)-sulfide particles. The total of the active sites on the promoted catalyst grows as compared to the unpromoted one because of an increase in "slow" sites. Evidently, the role of the "rapid" sites in catalyst functioning is dual: on the one hand, the sites increase catalytic activity, on the other - they encourage coke deposition of the catalyst. It is particularly important when processing heavy crudes. It is this dual role of "rapid" sites that we observe during residual hydrotreating on sample 7: the total mobile sulfur is high (actually is the same as in sample 5b), which leads to a high desulfurization activity, and a high P of some part of active sites results in strong coke formation. Thus, there seems to be some ground to state that when selecting most efficient catalysts for residual oil preliminary hydrotreating one should consider as preferable the systems with great amount of mobile sulfur. *i.e.* relatively high number of active sites and low productivity of these.

The study discussed in this paper has permitted us to put forward two catalysts - 7.4 % Co/ SiO_2 in its reduced form (sample 2a) and (3.4 % Co + 4.1 % Ni)/ Al_2O_3 in its sulfide form (sample 5b) as catalysts-adsorbents for the first stage of hydrotreating of heavy crudes. An important advantage of these catalysts is their relative cheapness due to the absence of expensive Mo in them.

CONCLUSIONS

- i. The present investigation gives us ground to state that when selecting most efficient catalysts for residual oil preliminary hydrotreating one should consider as preferable the systems with great amount of mobile sulfur. *i.e.* relatively high number of active sites and low productivity of these.
- ii. The study has permitted us to put forward two catalysts - (7.4 % Co)/ SiO_2 in its reduced form and (3.4 % Co + 4.1 % Ni)/ Al_2O_3 in its sulfide form as catalysts-adsorbents for the first stage of hydrotreating of heavy crudes. An important advantage of these catalysts is their relative cheapness due to the absence of expensive Mo in them.

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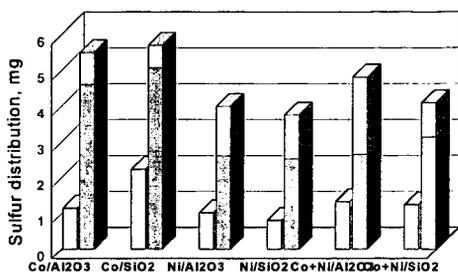


Figure 1. Sulfur distribution vs. catalyst composition and pretreatment procedure. Left bars - samples sulfidized by thiophene; right bars - by H_2S/H_2 . Light parts of bars - mobile sulfur; dark ones - immobile sulfur (see experimental conditions in Tables 1 or 2).

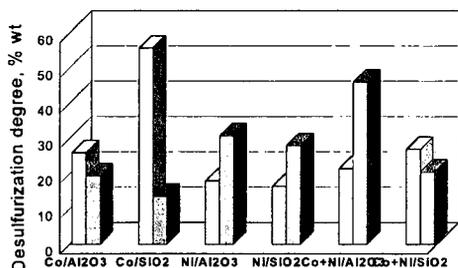


Figure 2. Desulfurization degree of residual oil vs. catalyst composition and pretreatment procedure. Left bars - reduced catalysts; right ones - sulfidized catalysts.

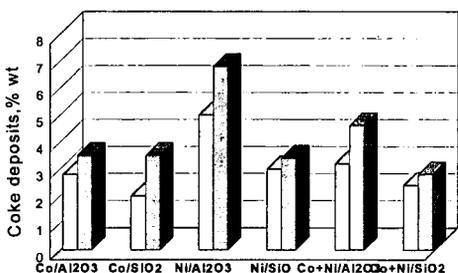


Figure 3. Coke deposition on the catalyst vs. composition and pretreatment procedure. Left bars - reduced catalysts; right ones - sulfidized catalysts.

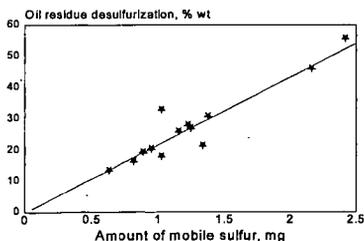


Figure 4. Oil residue desulfurization degree vs. amount of mobile sulfur on the catalysts under study.

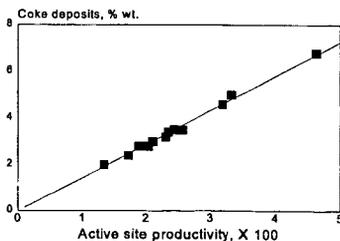


Figure 5. Coke deposition on the catalyst samples vs. active site productivity.

Table 1: Results of radioisotope testing of catalysts in the reaction of thiophene HDS (100 mg sample loading, 360°C, H₂ flow, pulses of thiophene-1-I)

No. smp	Catalyst composition	Pretreatment agent	S _{total} % wt	S _{mob} % wt	S _m /S _t %	*, % mol	P ^{**} 10 ²
1a	(7.0%Co)/Al ₂ O ₃	thiophene	1.16	1.16	100	5.40	1.89
1b	(7.0%Co)/Al ₂ O ₃	H ₂ S/H ₂	5.50	0.89	16.2	5.34	2.43
2a	(7.4%Co)/SiO ₂	thiophene	2.42	2.42	100	8.00	1.34
2b	(7.4%Co)/SiO ₂	H ₂ S/H ₂	5.70	0.63	11.1	4.00	2.56
3a	(7.6%Ni)/Al ₂ O ₃	thiophene	1.03	1.03	100	8.43	3.33
3b	(7.6%Ni)/Al ₂ O ₃	H ₂ S/H ₂	4.00	1.38	34.5	15.70	4.63
4a	(7.3%Ni)/SiO ₂	thiophene	0.82	0.82	100	4.25	2.10
4b	(7.3%Ni)/SiO ₂	H ₂ S/H ₂	3.76	1.23	32.7	7.25	2.34
5a	(3.4%Co+4.1%Ni)/Al ₂ O ₃	thiophene	1.34	1.34	100	7.62	2.30
5b	(3.4%Co+4.1%Ni)/Al ₂ O ₃	H ₂ S/H ₂	4.82	2.16	45.0	17.00	3.19
6a	(3.5%Co+3.5%Ni)/SiO ₂	thiophene	1.25	1.25	100	5.35	1.73
6b	(3.5%Co+3.5%Ni)/SiO ₂	H ₂ S/H ₂	4.10	0.95	23.2	4.15	2.03
7***	Ni-Mo/Al ₂ O ₃	H ₂ S/H ₂	6.08	2.49	41.0	59.00	20.1
							5.4

*) γ - thiophene conversion; **) P - active site productivity; ***) commercial catalyst

Table 2: Change of H₂S molar radioactivity (α) in the course of thiophene HDS on sulfide-³⁵S catalysts (100 mg sample loading, 360°C, H₂ flow, pulses of thiophene-1-I)

No smp	Catalyst	H ₂ S ^{MR}	No smp	Catalyst	H ₂ S ^{MR}
1a	Co/Al ₂ O ₃	= 100 exp(-1.23x)	4a	Ni/SiO ₂	= 100 exp(-1.74x)
1b	Co/Al ₂ O ₃	= 100 exp(-1.60x)	4b	Ni/SiO ₂	= 100 exp(-1.16x)
2a	Co/SiO ₂	= 100 exp(-0.59x)	5a	(Co+Ni)/Al ₂ O ₃	= 100 exp(-1.07x)
2b	Co/SiO ₂	= 100 exp(-2.26x)	5b	(Co+Ni)/Al ₂ O ₃	= 100 exp(-0.66x)
3a	Ni/Al ₂ O ₃	= 100 exp(-1.39x)	6a	(Co+Ni)/SiO ₂	= 100 exp(-1.14x)
3b	Ni/Al ₂ O ₃	= 100 exp(-1.04x)	6b	(Co+Ni)/SiO ₂	= 100 exp(-1.50x)
7	NiMo/Al ₂ O ₃	= 52.08 exp(-1.20x) + 47.92 exp(-0.32x)			

Table 3: Results of hydrotreating residual oil of West-Siberian petroleum (initial residual oil contained: asphaltenes - 4.3 %, S - 2.3 %, V - 40g/ton, Ni - 20 g/ton).

No smp	Catalyst composition	Pre-treatment*	Desulfur. degree, % wt.	Demetall. degree, % wt.	Residual asphaltenes % wt.	Coke deposits % wt.
1a	(7.0%Co)/Al ₂ O ₃	R	26.0	80.0	2.1	2.8
1b	(7.0%Co)/Al ₂ O ₃	S	19.4	80.0	2.0	3.5
2a	(7.4%Co)/SiO ₂	R	55.7	95.6	0.5	2.0
2b	(7.4%Co)/SiO ₂	S	13.6	89.0	1.3	3.5
3a	(7.6%Ni)/Al ₂ O ₃	R	18.0	82.0	1.2	5.0
3b	(7.6%Ni)/Al ₂ O ₃	S	30.8	80.0	2.0	6.8
4a	(7.3%Ni)/SiO ₂	R	16.5	90.5	1.0	3.0
4b	(7.3%Ni)/SiO ₂	S	28.0	78.0	1.8	3.4
5a	(3.4%Co+4.1%Ni)/Al ₂ O ₃	R	21.5	76.0	2.7	3.2
5b	(3.4%Co+4.1%Ni)/Al ₂ O ₃	S	46.0	61.0	3.8	4.6
6a	(3.5%Co+3.5%Ni)/SiO ₂	R	27.0	79.0	2.4	2.4
6b	(3.5%Co+3.5%Ni)/SiO ₂	S	20.5	76.0	2.6	2.8
7	(Ni+Mo)/Al ₂ O ₃ **	S	32.9	75.5	2.8	10.5

*) R - reduction; S - sulfidation after reduction; **) commercial catalyst