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## Two-Component Ni(Co)-Promoted MoS<sub>2</sub> Bulk Catalysts and Their Hydrodesulphurising Ability in Model Reactions and Diesel Fraction Hydrotreatment

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### Abstract

The paper deals with the solid-phase method for producing bulk two-component sulphide catalysts by the mechanochemical coupling of commercial molybdenum, cobalt, and nickel powders. The research presents physicochemical properties of the catalysts and discusses the activity of the latter in model reactions of dibenzothiophene and 4,6-dimethyldibenzothiophene hydrodesulphurisation including the latter in the presence of carbazole and phenanthrene, and also upon the hydrotreatment of sulphur components in diesel fraction.

**Key words:** bulk catalysts, powders, mechanical activation, hydrodesulphurising ability, hydrotreatment, model reactions, diesel fraction

### INTRODUCTION

There are a growing number of publications for bulk sulphide catalysts in the area of the hydrotreatment of oil fuel fractions [1, 2]. These are carrier-free catalysts with a high concentration of the active component. There is an increasing need for new catalytic systems because of the steady weighting of the extracted and processed oil raw materials [3, 4].

The literature has described in detail formulations of the synthesis of bulk sulphide catalysts for hydrotreatment using solid-phase mechanoactivation (MA) [5–7]. The products are MoS<sub>2</sub> and WS<sub>2</sub> sulphides in nanoscale condition. Straightfor-

ward methods for the preparation of bulk sulphide catalysts in one stage do not require an additional step of sulphidation and the use of solvent technologies. Therein lies the advantage of the use of the purified mineral molybdenite (MoS<sub>2</sub>) as a dimensional precursor of the active catalytic component. Conditions for the mechanical grinding of molybdenite that are given in literature sources usually correspond to the mode of the greatest contribution of impacts of shock nature compared to shear deformations. The specificity of MoS<sub>2</sub> as a representative of *d* transition metal dichalcogenide having a layered structure is poorly implemented under such conditions.

Meanwhile, as it is known, layered nanostructures of *d* transition metal dichalcogenides ( $2\text{H-MCh}_2$  where  $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Ch} = \text{S}, \text{Se}$ ) and their intercalation nanophases are promising to make multifunctional nanomaterials for various purposes. These are hydrogen-containing nanomaterials, hydrogen nanosensors, highly anisotropic semiconducting nanomaterials, solid nanolubricants, and also nanocatalysts [8–10].

We have earlier reported our developed straightforward one-step method for the preparation of nanoscale one-component  $\text{MoS}_2$ -catalytic systems under dry molybdenite grinding conditions at low values of grinding media acceleration ( $g \leq 50 \text{ m}^2/\text{s}$ ), for which the threshold effect of an increase in the activity in the model hydrogenolysis reaction of dibenzothiophene (DBT) was found [11 and 12]. The layered compound  $\text{MoS}_2$  is mainly exposed to longitudinal fragmentation under the investigated conditions, which leads to it leads to the layer-by-layer mixing of reagents in the mode of plastic deformations followed by the formation of nanoscale  $\text{MoS}_2$  crystallites.

As it is known, the hydrodesulphurising ability of supported catalysts for the hydrotreatment of diesel fractions, *e.g.*,  $\text{Ni}(\text{Co})\text{-Mo/W-S/Al}_2\text{O}_3$ , is substantially reduced in the presence of condensed polycyclic aromatic and heteroaromatic compounds [13]. That may be explained by the competitive adsorption of the latter by sulphur compounds over active catalytic sites. Similar data for bulk catalysts have been poorly reflected in the literature.

The objective of this research was the one-step synthesis of two-component  $\text{Ni}(\text{Co})\text{-MoS}_2$  systems by the solid-phase method, the determination of their physicochemical properties and hydrodesulphurising activity in model reactions of DBT and 4,6-dimethyldibenzothiophene (DMDBT) hydrogenolysis, including the latter in the presence of phenanthrene (PN) and carbazole (CB), and also upon the hydrotreatment of diesel fraction components.

## EXPERIMENTAL

### Starting materials

In order to obtain two-component catalytic systems, there were used the following materials: commercial coarse powders of molybdenum disulfide ( $\text{MoS}_2$ , DMI-7, obtained from the purified mineral molybdenite, an assay of 99.72 %), cobalt

(produced by electrolytic method for the purposes of powder metallurgy and magnet production, an average size of  $70 \mu\text{m}$ , GOST 9721–79, PC-1u grade), and nickel (produced by electrochemical deposition from aqueous solutions of metal salts followed by drying and thermal treatment in a reducing medium, a medium size of  $35 \mu\text{m}$ , TR 1793-001-07622839–2002, PNE-1 grade).

### Synthesis of catalysts and conditions for carrying out model reactions

Starting materials were exposed to MA under a vacuum of  $10^{-5}$  Torr in a KM-1 vibratory mill at a vibration frequency and amplitude of 16 Hz and 2 mm, correspondingly, with their varying mass ratios:  $\text{Co}(\text{Ni})/\text{MoS}_2$  (1 : 1, 1 : 3, 1 : 5, 1 : 7, 1 : 10) within a time interval of 0.5–24.0 h.

Experiments for the determination of the catalytic activity of the samples were carried out in a Autoclave Engineers Bolted Closure close-type reactor (a capacity of 100 mL) at a temperature of  $340^\circ\text{C}$ , a hydrogen pressure of 3.4 MPa, a mixing rate of 600 rpm, in a hexadecane solution (a volume of 80 mL) with reaction time,  $t = 8$  h. The initial concentration of DBT and DMDBT per sulphur was  $S_{\text{init}} = 500$  ppm. The activity of the catalytic systems was assessed according to the content of residual sulphur content ( $S_{\text{res}}$ , ppm) and transformation rate constants for DBT/DMDBT ( $k$ ,  $\text{h}^{-1}$ ). The model reaction in the presence of PN (500 ppm, the samples were dissolved in 80 mL of hexadecane) and CB (50 ppm per nitrogen) was also performed in the autoclave at  $340^\circ\text{C}$ , a pressure of 3.4 MPa (the excess amount according to  $\text{H}_2 = 4 : 1$ ) for  $t = 8$  h.

Apart from model reactions of hydrogenolysis, experiments were carried out with natural mixed raw materials. Mixed diesel fraction (DF) was prepared by mixing (90 mass % of the straight-run fraction + 10 mass % of the portion of catalytic cracking in the Ryazan refinery). Sulphur content in DF was 2.08 mass %, nitrogen – 184 ppm, a total content of aromatic hydrocarbons of 48.9 mass % (monocyclic + bicyclic + tricyclic compounds), a density  $0.8574 \text{ g/cm}^3$ . Prior to use, DF was diluted in hexadecane by 40.2 times, which corresponded to sulphur content,  $S_{\text{init}} = 500$  ppm, as in model reactions. The experiments were performed in a stationary autoclaving mode.

### Instrumental methods of research

**UV spectroscopy.** Changing DBT concentration in the intermediate samples to calculate rate constants for dibenzothiophene transformation

( $k$ , h<sup>-1</sup>) was determined using Uvikon-943 spectrophotometer (Kontron Instruments, Italy) analytical wavelength,  $\lambda = 324$  nm.

**Gas chromatography-mass spectrometry.** The composition of hydrodesulphurizates at the end of model reactions (8 h) was determined according to gas chromatography-mass spectrometry (GC-MS) data (NIST-5 computer mass spectral library) using Thermo Scientific DFS GC/MS system (Germany).

**X-ray fluorescence analysis** for the determination of sulphur content in DF hydrogenolysis and model reactions products was carried out using OXFORD Instruments Lab-X 3500 SCL analyser.

**Electronic microscopy.** Surface morphology of the catalysts was determined by transmission electronic microscopy (TEM) using Philips CM-30 (Netherlands) and JEOL JEM-2010 (Japan) instruments.

**X-ray diffraction (XRD) analysis** was conducted using Discover D8 diffractometer (Bruker, Germany) in an angle range of 8–46 deg, with monochromatic CuK $\alpha$ -radiation. Nanocrystallite sizes,  $L$  (the length of basal faces) were determined according to coherent scattering regions (CSR) of the samples. The values of interplanar distances ( $D_{002}$ ) were determined using the Debye – Scherrer equation. The data were mathematically processed using the PDF-4+ powder database of the International Centre for Diffraction Data (ICDD).

**Monitoring for changing magnetic properties** of the initial reaction mixtures and the mechanically activated products was performed according to magnetization curves (changing saturation magnetization) that were recorded using a Faraday balance.

## RESULTS AND DISCUSSION

One of the most crucial factors that determines the activity of the catalyst and the composition of reaction products is a quantitative ratio of components that comprise the catalytic agent. The preliminary screening of the samples (Table 1) with the most apparent hydrodesulphurising activity in relation to sulphur-containing model compounds (DBT and DMDBT) has demonstrated the following results. In Co-containing AK-25 and AK-47 samples prepared at  $t_{MA} = 8$  h and mass ratios of 1 : 7 and 1 : 10 (atomic ratios of 1 : 2.6 and 1 : 3.8, Co/Mo = 0.4 and 0.3, respectively), the minimum residual sulphur content in a series of the Co-catalysts given is  $S_{res} = 25$  and 26 ppm. The difference in the composition of products for AK-25 and AK-47 samples is manifested in some increase of the content of biphenyl (BP) between ~ 77 and 86 % for and a synchronous decrease in the concentration of cyclohexylbenzene (CHB) from ~ 23 to 14 %. Therefore the conversion is mainly carried out *via* the “cracking” route under

TABLE 1

Two-component catalytic systems in the model hydrogenolysis reaction of dibenzothiophene (DBT).  $S_{init} = 500$  ppm, a temperature of 340 °C, a pressure of 3.4 MPa (an excess according to H<sub>2</sub> = 4 : 1), reaction time of 8 h

Sample code	Composition	Co(Ni) + MoS <sub>2</sub> /Mo ratio		MA time, h	S <sub>res</sub> , ppm	k, h <sup>-1</sup>	Products			
		Mass	Atomic <sup>1</sup>				BP	CHB	THDBT <sup>3</sup>	
AK-54	Co/MoS <sub>2</sub>	1 : 1	1 : 0.4	4	409	0.15	79.13	19.56	1.31	
AK-55		1 : 3	1 : 1.1	4	144	0.25	83.41	16.37	0.22	
AK-66		1 : 5	1 : 1.9	4	62	0.85	57.76	42.24	–	
AK-67		1 : 5	1 : 1.9	8	92	0.49	81.8	18.2	–	
AK-65		1 : 7	1 : 2.6	4	31	0.88	51.58	48.42	–	
AK-25		1 : 7	1 : 2.6	8	25	0.68	77.21	22.79	–	
AK-56		1 : 10	1 : 3.8	4	53	1.65	78.61	21.39	–	
AK-47		1 : 10	1 : 3.8	8	26	0.64	86.32	13.73	–	
AK-57		Ni/MoS <sub>2</sub>	1 : 7	1 : 2.6	4	30	0.62	74.30	25.70	–
AK-49			1 : 7	1 : 2.6	8	87	0.29	53.88	46.12	–
AK-58	1 : 10		1 : 3.7	4	15	0.60	30.70	69.31	–	
AK-50	1 : 10		1 : 3.7	8	117	0.25	74.54	24.98	0.48	
AK-58* <sup>2</sup>	1 : 10		1 : 3.7	4	15	0.74	19.21	59.70	21.09	

Note. The dash indicates that the quantity of THDBT is less than 0.0026 %.

<sup>1</sup> Atomic Co(Ni)/Mo ratio in Co(Ni)/MoS<sub>2</sub> systems.

<sup>2</sup> AK-58\* – 4,6-dimethyldibenzothiophene (DMDBT) as model compound.

<sup>3</sup> THDBT stands for tetrahydrodibenzothiophene.

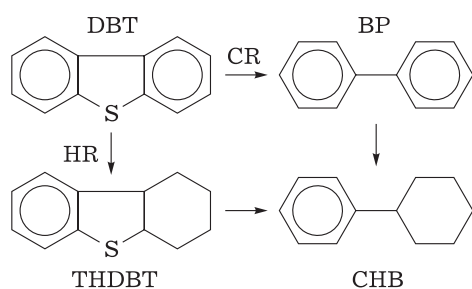


Fig. 1. Reaction scheme for dibenzothiophene (DBT) hydrogenolysis. THDBT, BP, and CHB are tetrahydrodibenzothiophene, biphenyl, and cyclohexylbenzene, respectively; CR and HR are cracking and hydrogenation routes, correspondingly.

the investigated conditions (Fig. 1) by the breaking of the C–S bond to form BF followed by its hydrogenation to CHB.

The first systematic investigations of the activity of catalytic systems containing CoMo and NiMo oxide precursors supported onto alumina [14] considered the issue of catalytic activity as a function of the atomic Co(Ni)/Mo ratio. As determined, the promoter effect in the supported catalysts was largely apparent at atomic Co/Mo ratios of 0.3, and for Ni/Mo – 0.6. The specified values almost match for bulk catalysts (see Table 1) for Co (0.4–0.3 for AK-25, for example, 1/2.6 ~0.4) but twice lower for Ni (0.3).

The optimum mechanical activation time for Ni-containing systems is 4 h. Changing the component mass ratio between 1 : 7 (AK-57) and 1 : 10 (AK-58) or a decreased promoter fraction from 1 : 2.6 to 1 : 3.7; see Table 1) leads to an increased desulphurisation depth ( $S_{\text{res}} = 30 \text{ ppm} \rightarrow 15 \text{ ppm}$ , respectively). Herewith, the quantity of BP in the product is reduced by 2.5 times, but the presence of cyclohexylbenzene is increased in the series CHB = 26  $\rightarrow$  46  $\rightarrow$  60  $\rightarrow$  69 % (for catalysts AK-57  $\rightarrow$  AK-49  $\rightarrow$  AK-58\*  $\rightarrow$  AK-58). These trends for AK-58\* and AK-58 samples attest to an increase in the contribution of the hydrogenation reaction route. The values of reaction rate constants for those specimens are 0.60 and 0.74  $\text{h}^{-1}$ , correspondingly ( $S_{\text{res}} = 15 \text{ ppm}$ , see Table 1). It is worth noting that these two samples (AK-58\* and AK-58) represent the outcome of desulfurisation of DMDBT and DBT, respectively. According to the literature data, 4,6-dimethyldibenzothiophene is referred to especially stable sulphur compounds under hydrotreatment conditions. The outcome that deals with the same degree of hydrodesulfurisation for both model compounds under the investigated conditions has already been described in literature sources. In addition,

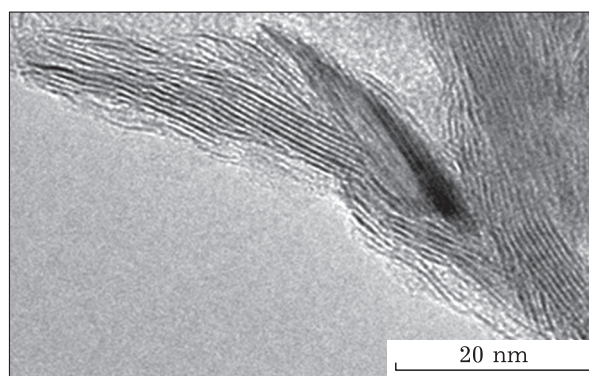


Fig. 2. TEM image for Co(Ni)/MoS<sub>2</sub> systems.

AK-58\* sample (see Table 1) as an intermediate desulfurisation system is notable for increased content of THDBT (21%). This experimental fact indicates an even higher contribution of the hydrogenating ability of the catalyst and, perhaps, even more exhaustive hydrodesulphurisation ( $S_{\text{res}} < 15 \text{ ppm}$ ) with increased reaction time.

There are no metal nanoparticles in the TEM image according to Fig 2. However, the layered structure of molybdenite is preserved after MA. At the same time, the profiles of diffractograms (Fig. 3, a and b) have reflexes that correspond to Ni and Co metals, and also to MoS<sub>2</sub> in two-component catalysts (Table 2, catalysts 4 and 5 and Table 1, AK-58 and AK-25 samples).

It is particularly noteworthy that only reflexes related to MoS<sub>2</sub> and Co(Ni) phases have detected by X-ray phase analysis (XPA). Herewith, mixed sulphidic Co(Ni)–S/MoS<sub>2</sub> or Co(Ni)–S phases have not been found. This conclusion is legitimate to make on the basis of variations in the magnetization of the starting materials and the MA of the catalysts based on them. This indicates that there is no topochemical resulphuration of the protector as previously discovered for the three-component MoS<sub>2</sub> + Co(Ni) + nanodiamonds system [15].

As indicated by XRS spectra data processing (see Table 2), linear dimensions,  $L$ , the interplanar distances,  $D_{002}$ , the internal elastic micro-stresses,  $\Delta d/d$ , and the parameters of elementary cells,  $c/a$ , of promoter-containing MoS<sub>2</sub> nanocrystallites are changed, which reflects the defectiveness level.

There are the following similarities and differences for the samples after the mechanoactivation of molybdenite and two-component samples obtained at a mechanical treatment time of 4 and 8 h (see Table 2).

For a mechanical activation time of 4 h, the average length of the basal faces of crystals  $L$  of the initial MoS<sub>2</sub> (0) molybdenite is reduced by

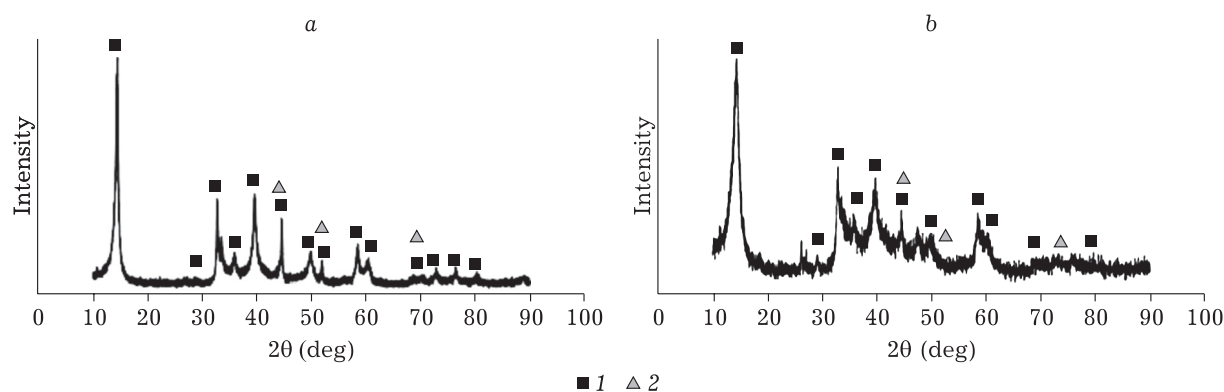


Fig. 3. XRD patterns of catalysts: a – AK-58, Ni/MoS<sub>2</sub> = 1 : 10,  $t_{MA}$  = 4 h; b – AK-25, Co/MoS<sub>2</sub> = 1 : 7,  $t_{MA}$  = 8 h; 1 – reflexes related to Mo; 2 – reflexes of Co/Ni promoters.

TABLE 2

Structural parameters of the samples and their hydrodesulphurising ability in relation to dibenzothiophene

Entry	Catalysts	Mechanical activation time, h	XRS data				$k$ , h <sup>-1</sup>	$S_{res}$ , ppm
			$L$ , nm	$D_{002}$ , Å	$\Delta d/d \cdot 10^3$	$c/a$		
1	MoS <sub>2</sub> (0)	0	50	6.15	2.1	3.888	0.22	405
2	*MoS <sub>2</sub> (4)	4	20	6.15	2.6	3.909	0.08	385
3	*MoS <sub>2</sub> (8)	8	12	6.20	8.8	3.954	0.46	105
4	Ni/MoS <sub>2</sub> = 1 : 10	4	21	6.19	7.2	3.914	0.74	15
5	Co/MoS <sub>2</sub> = 1 : 7	8	10	6.21	8.5	3.951	0.88	25

Note. \*MoS<sub>2</sub> (8) – molybdenum disulphide mechanoactivated for 8 h.

2.5 times and equals to 20 and 21 nm for samples \*MoS<sub>2</sub> (4) and Ni/MoS<sub>2</sub> = 1 : 10, respectively. The values of the length of the basal faces of nanocrystallites formed during MA for 8 h are also close:  $L$  = 12 nm for \*MoS<sub>2</sub> (8) and  $L$  = 10 nm for the Co/MoS<sub>2</sub> = 1 : 7 sample. Thus, it can be assumed that the presence of the promoter has no significant effect on the fragmentation of the basal faces of nanocrystallites. To a greater extent, the effect of this type is typical for changing mechanical activation time.

The observed differences in changes of interplanar distances in crystallites are also not so significant: a range of 6.15–6.21 Å.

According to the data listed in Table 2, there is an increase of internal elastic strain ( $\Delta d/d \cdot 10^3$ ) between 2.1 and 8.8, like microstrains in elemen-

tary cells within a range between 3.888 and 3.954 for reference samples of molybdenite (MoS<sub>2</sub>) itself (No 1–3) without promoters ( $t_{MA}$  = 4 and 8 h). Alongside with that, it is worth noting that the Ni-containing sample ( $S_{res}$  = 15–16 ppm) has the highest activity in a series of two-component catalysts. Changing structural parameters for the specified sample is insignificant (see Table 2).

#### Activity of two-component systems in the presence of carbazole and phenanthrene

It follows from the data shown in Table 3 that in the absence of model nitrogenous and aromatic compounds (CB and PN) the hydrodesulphurising activity of the Ni-containing catalyst is by 1.5 times higher compared to that over the Co catalytic agent. The higher activity may be due to the

TABLE 3

Hydrodesulphurising ability of two-component catalysts in the model reaction of dibenzothiophene (DBT) hydrogenolysis in the presence of carbazole (CB) and phenanthrene (PN), ppm

Catalysts	Residual sulphur content $S_r$ in model mixtures			
	DBT	DBT + PN	DBT + CB	DBT + PN + CB
Co/MoS <sub>2</sub> = 1 : 7, $t_{MA}$ = 8 h	25	16	133	24
Ni/MoS <sub>2</sub> = 1 : 10, $t_{MA}$ = 4 h	15	15	136	15

greater contribution of the hydrogenation ability for the N-promoted sample (see Fig. 1 and Table 1, AK-58, 70 % of CHB). The model reaction then proceeds *via* two paths, *i.e.* cracking and hydrogenating. In due turn, that leads to the lower content of residual sulphur in the products.

A new effect was found in the model reaction with DBT when introducing PN into the reaction mixture (see Table 3). The essence of the former consists in the fact that PN does not have an effect on the hydrodesulphurising activity of the Ni-containing catalyst but leads to an increase in the strength of the Co-containing sample ( $S_{\text{res}}$  is reduced by 1.6 times, between 25 and 16 ppm). At the same time, when CB is added to the reaction mixture, the hydrodesulphurising ability of the both catalysts is equally reduced, which is in full agreement with the literature data [13]. When both PN and CB are present in the reaction mixture at the same time, there is no decrease in catalytic activity. In other words, PN as a condensed aromatic compound almost completely neutralizes the inhibiting effect of CB as a model heteroatomic compound. The cause of such an effect is not clear so far.

Thus, conditions, wherein aromatic compounds do not have an effect on the hydrodesulphurising ability of two-component bulk catalysts, have been found. The effect of PN as an inhibitor of the negative impact of nitrogenous compounds has been discovered in the presence of new bulk two-component sulphide catalysts.

#### *Hydrodesulphurising ability of Ni/MoS<sub>2</sub> catalyst in relation to sulphur components in diesel fractions*

This step of research involved the use of a mixture of the straight-run diesel fraction (90 %) and hydrocracking one (10 %) from the Ryazan refinery instead of model compounds, such as DBT and DMDBT. An aliquot of DF was added to hexadecane in such a way that sulphur was present in the tested solution in an amount of 500 ppm as in the model reactions. After the hydrodesulphurization of the reaction mixture based on DF for the two-component system Ni/MoS<sub>2</sub> = 1 : 10, the level of  $S_{\text{res}}$  = 44 ppm. It is worth noting that a decreased sulphur content by more than 11 times takes place under conditions of the minimum excess according to H<sub>2</sub> (4 : 1), whereas conventional hydrotreatment conditions assume an excessive amount for hydrogen by 200–1200 times [13]. This indicates significant potential opportunities

for the practical use of the investigated two-component catalysts.

#### CONCLUSION

It has been shown for the first time that two-component sulphide catalysts may be obtained in one step by the solid-phase mechanochemical coupling of commercial micron molybdenite, nickel, and cobalt powders. The optimum promoter/active component ratios have been determined. The positive synergism for such catalytic systems has been found using phenanthrene in hydrodesulphurisation reactions of a model mixture of dibenzothiophene, phenanthrene and carbazole. The former completely eliminates the presence of carbazole and increases the hydrodesulphurising ability of the Co-containing system. As shown, the higher activity of Ni-containing catalysts is due to their high hydrogenating ability. Herewith, there is no correlation between defectiveness and catalytic activity. The outcome acquired for the Ni/MoS<sub>2</sub> system using the mixed diesel fraction as a model indicates the prospects for such catalysts.

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