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Sulfide Catalysts for Hydropurification of Oil Fractions

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Abstract—Analysis of the literature on catalysis by transition metal sulfides is carried out. Problems which now can be considered solved, and unsolved problems are marked. Catalysts such as Co(Ni)Mo(W) on thermostable oxides are considered. Arguments in support of the hypothesis about formation in the oxide precursors of all this type catalysts of heteropoly compounds (HPC) of Mo(W) are considered. The formation of HPC occurs at the hydrothermal stage of the synthesis of the catalysts under contact of Mo(W) atoms and complexing agents in an acid medium. The role of the complexing agent can be played by atoms of the support (Si, Al, Ti, etc.) or atoms of the modifying additive.

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INTRODUCTION

Various facets of hydropurification and catalysis by transition metal sulfides are abundantly documented. Statistical analysis of about 9000 of scientific papers and patents published over the past two decades, performed by Parlevliet and Eijsbouts [1] by a special program (AnaVist, STN) showed that transition metal sulfides have been widely used as catalysts.

Catalytic processes in a hydrogen medium, first of all hydropurification, have become quiter common in large-scale secondary oil refining technologies. Hydropurification is aimed at improving the quality of distillates by removing sulfur, oxygen, nitrogen, and resins via catalytic hydrogenation of unsaturated compounds with hydrogen at elevated temperatures. In the fuel production industry, hydropurification is used for preparing raw material for isomerization, reforming, and catalytic cracking and for purification of reactive and diesel fractions. Hydropurification of diesel fuel is the most large-scale process, and most scientific publications are devoted to the chemistry, technology, and catalysts of this process. Even though there have been considerable advances in this field, hydropurification in oil refining still attracts enduring and growing interest. This is explained by such objective factors as increasing fraction of sulfur and high-sulfur oils, demand for deeper oil refining, and strengthening requirements to oil product quality [2].

According to the EN 590 specifications, beginning with 2008 the total sulfur in diesel fuels should not be higher than 10 ppm (PAH ≤ 2 wt); in Sweden, the 1st class fuel should not contain more than 1 ppm of sulfur and 0.02 wt % of PAH. By 2010 all diesel motor cars in EU countries will start to use an almost sulfur-free fuel. In the USA, 80 % of oil refineries are able to start production of ultra low sulfur diesel (ULSD) already at present and the rest 20%, by 2010 [3]. The modern high-quality oil production technology involves hydropurification [4].

For deeper oil refining into commercial products, a growing number of uses are being found for fractions obtained by thermocatalytic (destructive) processes. For example, light catalytic cracking gasoil, visbreaking or thermobreaking gasoils, and delayed coking gasoil are used in the production of diesel fuels [5, 6]. Secondary distillates which contain a large fraction of unsaturated hydrocarbons (aromatic, olefinic, dienic, etc.), resins, and hardly removable cyclic sulfur compounds are less readily hydrogenated than direct distillates.

Figure 1 shows operational data from an installation for hydropurification of diesel fuel. The feed was a mixture of the direct fraction and coking and catalytic cracking gasoils. As seen from the figure, as the sulfur content in the secondary gasoils increases from 15 to 36 wt %, the desulfurization degree decreases from ~96.5 to 92 rel %. Obviously, the applied catalyst and process conditions do not allow a hydrogenizate with the total sulfur content of about 50 ppm, not to mention 10 ppm, at which desulfurization degrees of respecitively 99.6 and 99.9 rel % are attainable.

The reactivity of organosulfur compounds in oil decreases in the following order: thiols > disulfides > sulfides ≈ thiophanes > thiophenes > benzothiophenes (BT) > dibenzothiophenes (DBT) [7–10]. When monosubstituted BT are removed completely, the degrees of removal of monosubstituted DBT and 4,6-diethyldibenzothiophene (4,6-DMDBT) are 95 and 83 rel %, respectively [11]. In the presence of Co(Ni)Mo/Al_2O_3 catalysts, dibenzothiophene is 5–6 times more reactive than 4,6-DMDBT [12]. According to [2], in hydropurified diesel fractions with residual sulfur contents of 0.05 wt %, thiophene derivatives make 98.0–99.5% of sulfur compounds. At a deeper degree of hydropurification of diesel fractions, the remaining sulfur compounds are more and more difficult to remove.

To select catalysts for deep hydropurification of diesel fuel, we have studied the chemical composition of 22 fractions, of which 14 resulting from direct distillation, 6 from thermal or thermocatalytic processes, and 2 were a mixed raw material of the hydropurification process [13]. The total sulfur contents of these fractions varied from 0.78 to 1.13 wt % (Tables 1 and 2). The PAH concentrations in the direct fractions were 5.7–8.8 wt %, in the secondary fractions, 16.6–18.1 wt %, and the mixed raw material contained a moderate quantity of PAH (6.6 wt %). Thiophene derivatives comprised 82.4 to 91.1% of total sulfur (Table 2). The fraction of thiophene derivatives in the fraction 240–350°C, by data for 1988 [14], was 57.2% of the total sulfur. It is seen from the presented data that the hydropurification of mixed raw material with high contents of thiophene derivatives and PAH to residual total sulfur contents of lower than 10 ppm is not a trivial task.

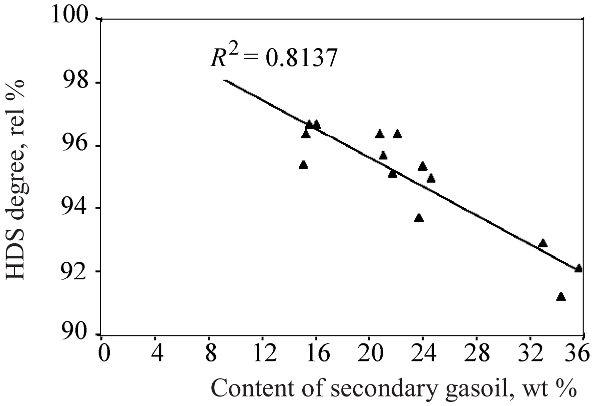

Fig. 1. Desulfurization degree vs. content of secondary gasoil in raw material.

Structure of the Active Phase of Hydropurification Catalysts

Catalysts for hydropurification of different kinds of oil stocks are based on a universal composition: Co(Ni)Mo(W)S on a support whose role until present time has almost exclusively been played by γ-Al_2O_3. The versatility and universality of this system has favored to the creation by the end of XX century of hundreds brands of commercial hydropurification catalysts fully satisfying the demand of industry. Therefore, an opinion has formed [15, p. 481] that

Table 1. Chemical composition of certain medium oil fractions and mixed hydropurification raw material

Fraction	Sulfur, wt %	Aromatic hydrocarbons, wt %				
		monocyclic	bicyclic	tricyclic		PAH
				phenanthrene	anthracene	
Fraction 240–350°C	0.86	14.5	3.9	2.5	0.02	6.5
Fraction 240–350°C	0.78	14.5	4.2	1.4	0.05	5.7
Fraction 270–365°C	1.35	18.6	4.1	4.3	0.43	8.8
Light catalytic cracking gasoil	0.92	36.9	12.6	5.5	—	18.1
Light catalytic cracking gasoil	1.10	32.1	10.9	5.7	—	16.6
Mixed hydropurification raw material	0.91	16.2	5.0	1.6	—	6.6

Table 2. Group composition of sulfur compounds in hydropurification raw material

Fraction	Sulfur, wt %						Fraction of thiophene sulfur, %
	total	H_2S	RSH	RSSR	RSR	thiophene derivatives	
Fraction 240–350°C	1.13	0.02	0.01	0.13	0.03	0.94	83.2
Fraction 270–365°C	1.75	0.00	0.00	0.19	0.02	1.55	88.1
Light catalytic cracking gasoil	1.46	0.07	0.01	0.09	0.00	1.30	88.8
Light catalytic cracking gasoil	1.48	0.03	0.08	0.09	0.02	1.25	84.9
Light coking gasoil	1.84	0.00	0.04	0.08	0.05	1.68	91.1
Mixed hydropurification raw material	1.39	0.02	0.08	0.13	0.01	1.15	82.4

there are almost no reasons for developing new catalysts of this type.

However, the advent of more stringent requirements to fuel gave impetus to the development of new commercial hydropurification catalysts many times more active than the best catalysts in 1980s. These advances were made possible due to the development of physicochemical methods of investigation of catalysts, including *in situ* techniques [16]. The chemistry of sulfide catalysts is quite a complicated issue, and, even though powerful physicochemical methods of investigation are presently available, problems to be solved still remain [17].

How fully one can answer to two principal questions: "What is the structure of the catalyst?" and "How this structure affects the catalytic activity?" can serve as an indicator of the degree of knowledge of a heterogeneous catalyst [18, p. 249]. Different models of active phase, such as the monolayer, intercalation, remote control, facet–hoop, and other models, have been compared, and their correlation with experimental observables has been discussed in the literature since 1980s [19, 20] until present [21]. Topsoe and co-workers [22–27] established that the most active component of $Co(Ni)Mo(S)/Al_2O_3$ catalysts are small MoS_2 crystallites formed as short layered packings. The active catalytic centers are Co(Ni) atoms linked to the surface of these crystallites by sulfide bridges. This model was given the name "Co–Mo–S" phase. As shown in [28, 29], promoter atoms occupy edge sites at the MoS_2 "support." Later further evidence for the occurrence of Co–Mo–S structures was provided [7, 30]. The Co–Mo–S-phase model is now almost commonly accepted. Similar structures were also found in sulfidized $NiW/\gamma\text{-}Al_2O_3$ [31] and $NiMo/\gamma\text{-}Al_2O_3$ [28] catalysts.

Startsev and co-workers [21, 32] suggested a model of a sulfide bimetallic compound, which is a version of the "Co–Mo–S" model as applied to a carbon support (sibunite).

Depending of the type of interaction with the catalyst, the Co–Mo–S phase can be present as type I or type II structures with different catalytic properties [22, 33–35]. The Co–Mo–S phase of type I is formed by low-temperature sulfidation (<400°C). It is attached to the Al_2O_3 surface by Mo–O–Al anchor bonds [36]. High-temperature sulfidation leads to cleavage of Mo–O–Al bonds (type II phase). The most active commercial hydropurification catalysts contain type II phase.

In catalysts with a type II phase one can observe a "multilayer" MoS_2 structure. It is suggested [37] that monolayer MoS_2 clusters with edge Co atoms probably for a Co–Mo–S phase of type I, whereas multilayer MoS_2 clusters with Co not included into the base layers form a phase of type II. According to an alternative opinion [38], the multilayer packing is a "side effect" of weak cluster–support interactions. It is important to note that the top layer of the multilayer stack contains specific edge centers which play a key role in hydrogenation reactions. Thus, the morphology of MoS_2 clusters, specifically proportions of the layered structure (i.e. cluster side length/thickness ratio), as well as the size ratio of the crystallite and sulfur compound molecule exert a strong impact on catalytic transformations irrespective of whether promoters (Co or Ni) are present.

Furthermore, Iwata et al. showed [39] that the industrial hydropurification process involves destruction of the initially formed multilayer crystallites and stabilize monolayer MoS_2-like nanoparticles. As shown by quantum-chemical computations [40], the nature and concentration of active centers and the shape of MoS_2 crystallites can strongly vary with the chemical potential of the medium they reside in.

The catalytic action of Co–Mo–S structures is also dependent on the orientation of MoS_2 clusters on the support [37]. Top edge centers on edge-bound MoS_2 clusters which are perpendicular to the support surface weaker interact with the support than monolayer basal-bound MoS_2 clusters (parallel to the support). Moreover, top edge centers on edge-bound MoS_2 clusters are sterically less hindered that top centers on basal-bound MoS_2 clusters or edge centers on the base of basal-bound multilayer MoS_2 clusters.

Scanning tunnel microscopy (STM) makes it possible to observe MoS_2 [41], Co–Mo–S [25], and Ni–Mo–S [26] nanoclusters (Fig. 2) at an atomic resolution level. According to STM data, cobalt atoms in Co–Mo–S nanoclusters in hydrodesulfurization catalysts prefer to localize on the S-edges of truncated MoS_2 crystals (so called “S edges”) and affects the electronic state of neighboring sulfur atoms [25].

In one of their early works Lipsch and Schuit [42] suggested that the active centers are sulfide vacancies, and this suggestion was supported by many researchers (see, for example, [43]). As shown in [44–46], the ability to form anionic vacancies (due to removal of surface sulfur) correlates with catalytic activity. The nature of hydrogenation centers is not quite clear [9], but, here, too, vacancies are probably involves.

According to the results of DFT computations of the MoS_2 and Co–Mo–S structures [47], the energy of the Mo–S bond is of primary importance for catalytic activity. The promoting activity of Co was explained by a decrease of the Mo–S bond energy, and, as a consequence, an increase of the number of active centers (obviously, sulfide vacancies formed in a hydrogen medium).

Unlike commercial sulfide catalysts which are difficult to characterize, mixed dispersed transition metal sulfides have readily determined surface and volume properties. For this reason, such simple model catalysts as dispersed binary or ternary sulfides without a carrier may prove useful to study. Hensen et al. [48] have studied the activity of various transition metal sulfide in the thiophene hydrodesulfurization (HDS) reaction. It was suggested that the energy of the

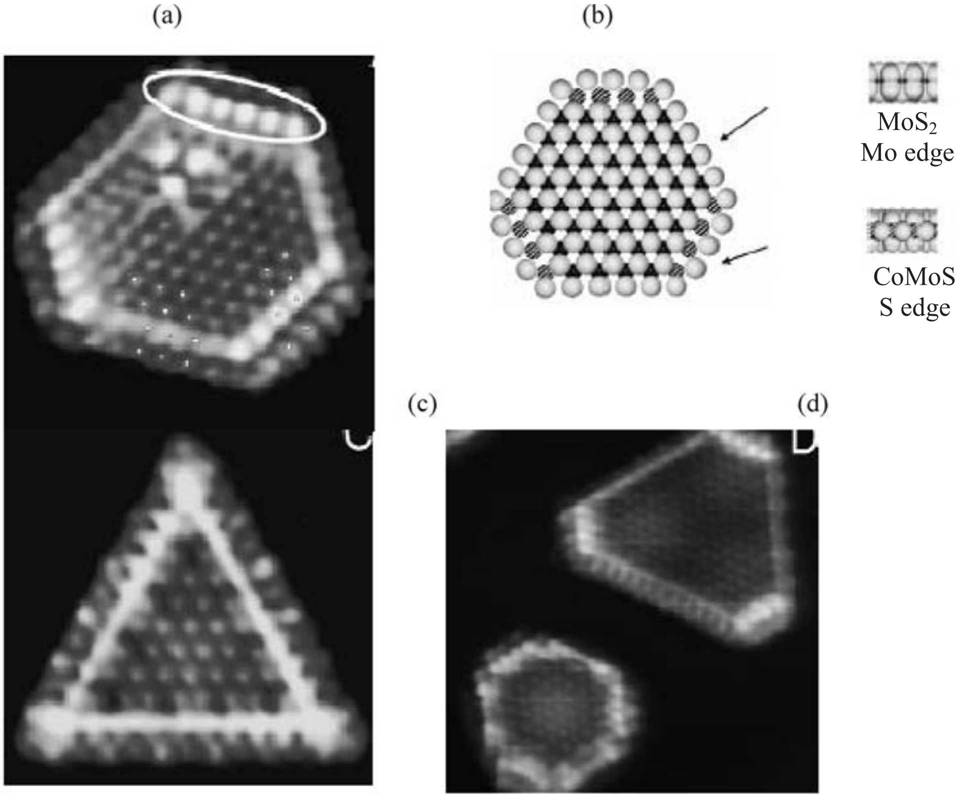

Fig. 2. Scanning microscope images of (a) Co–Mo–S, (c) MoS_2, and (d) Ni–Mo–S nanoclusters [26]. (b) Ball model of a Co–Mo–S monolayer.

metal–sulfur bond on the surface of a sulfide cluster depends on the number of metal–sulfur coordination bond and on the position of the metal in the Periodic Table.

According to Thiollier et al. [49], sulfur mobility is the key parameter responsible for catalyst activity in HDS and hydrogenation. The highest activity among model catalysts MCr_2S_4 (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, 2Na) was found to be characteristic of $CoCr_2S_4$ and $NiCr_2S_4$. Catalytic activity was correlated with reproducibility which was defined as the quantity of sulfur, removed from catalysts with hydrogen at 573 K. The promoting effect (main element Cr, promoter M) was explained in terms of different bond energies of sulfur with the active phase.

It was shown by SEM [26, 50] that sulfide clusters can contain active centers which are not sulfide vacancies but represent centers fully coordinated with sulfur and exhibiting metal-like properties.

Adsorption of Sulfur Compounds and Reaction Pathways

The concept of “defectless” heterogeneous catalysis (Startsev and co-workers [21, 32, 51]) suggests lacking anionic vacancies and involvement of “occluded” hydrogen.

The dynamics of active centers and the mechanism of hydrodesulfurization on sulfide Co–Mo catalysts applied on carbon or Al_2O_3 supports was studied by Kogan et al. by means of radioisotope techniques [52–57]. According to the results of Isagulyants et al. [52] on the hydrogenolysis of thiophene on ^{35}S-labeled MoS_2 and sulfidized Co–Mo/Al_2O_3, the formation of H_2S in both cases involves the catalyst sulfur atom which is substituted by the thiophene sulfur. It was shown that the Co–Mo/Al_2O_3 catalyst contains two types of sulfide sulfur with different reactivities [52]. Topsoe and Topsoe [58] reported evidence for the presence of SH groups in sulfidized catalysts. It was suggested that SH groups can serve as a source of hydrogen in the catalytic cycle. The concept of dynamically formed active centers was confirmed by Thiollier et al. [49].

Aliphatic thiols, sulfides, and disulfides readily enter HDS reactions in the presence of hydrogen and a catalyst; therewith, homolytic C–S bond cleavage takes place, and free valences are saturated with hydrogen. The reaction products are a saturated hydrocarbon and H_2S [59]. Thiophene derivatives are more stable organosulfur oil components, and, therefore, thiophene is frequently used as model in catalyst activity studies.

The first mechanistic concepts of thiophene hydrogenolysis suggested intermediate formation of tetrahydrothiophene [59, p. 285]. In the case of the MoS_3 catalyst, tetrahydrothiophene formation was confirmed experimentally. However, with catalysts like CoMo/Al_2O_3, no tetrahydrothiophene was found among the reaction products.

Certain evidence for the possibility of C–S bond cleavage in thiophene in the presence of hydrogen but without saturation of two double bonds was reported in [59, p. 285]. Later Amberg and co-workers [60, 61] obtained evidence for C–S bond cleavage with buta-1,3-diene formation. Their results showed that hydrogenated thiophene with intact C–S bonds (tetrahydrothiophene) gives hydrodesulfurization products differing from those with thiophene. The reaction scheme based on these and other data [42, 62, 63] was given in [15, p. 486].

Later three pathways of thiophene hydrogenolysis were discussed: (1) sulfur abstraction and formation of hydrogen sulfide and butadiene; (2) exhaustive hydrogenation of the thiophene ring followed by C–S bond cleavage; and (3) partial hydrogenation of thiophene, sulfur abstraction as hydrogen sulfide, and formation of butenes. The three pathways combined in a common scheme are presented in [7].

According to SEM data [42, 62, 63], the mechanism of thiophene hydrodesulfurization may be radically different. In particular, it was shown that thiophene molecules can be activated by hydrogen addition across one of the two double bonds to form a carbon-centered 2-hydrothiophene radical. Reaction pathways (hydrogenation and direct HDS) were discussed by Topsoe and co-workers [64] who suggested that the hydrogenation pathways involving intermediate formation of a carbon-centered 2-hydrothiophene, followed by 2,5-dihydrothiophene formation and S–C bond cleavage can occur at an equilibrium Mo edge without formation of coordinately unsaturated centers (Fig. 3, bottom part of the scheme). It was also found that the hydrogenation pathways can also be realized on the crystallite S edge (Fig. 3, bottom part of the scheme). However, in the latter case the initial equilibrium structure is unreactive, and sulfide vacancies should form to initiate reaction. Sulfide vacancies on the S edge, too,

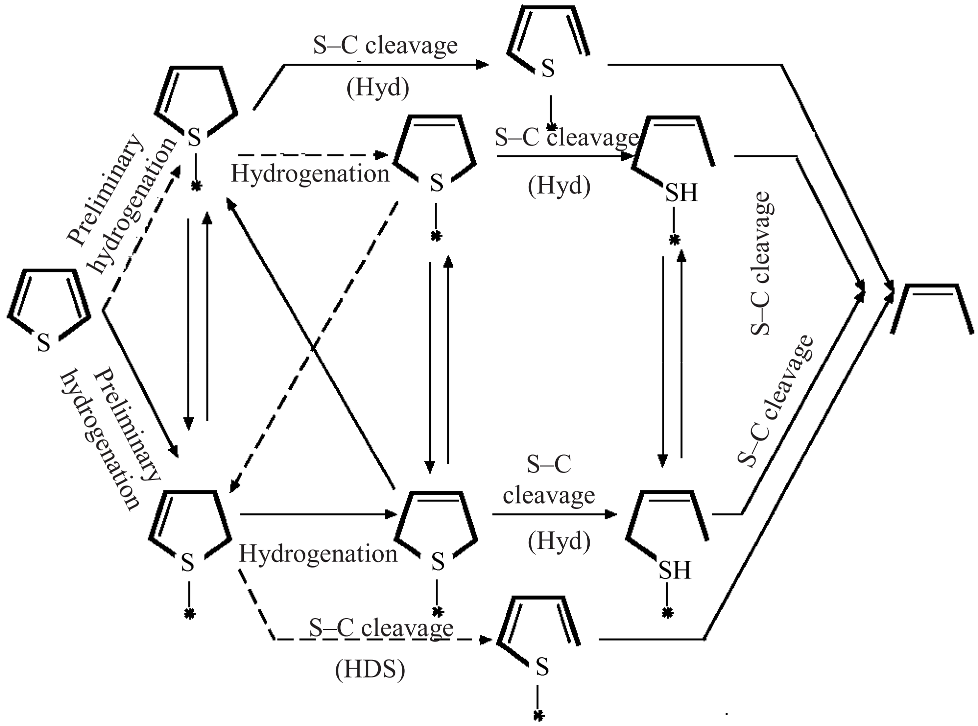

Fig. 3. Mechanism of thiophene hydrolysis [65]. (Dashed lines) Slow reactions; (Hyd) hydrogenation pathway; and (HDS) direct hydrodesulfurization pathway.

can serve as active centers in the direct hydrodesulfurization pathway. This pathway, too, involves formation of a carbon-centered 2-hydrothiophene radical but involves no 2,5-dihydrothiophene formation [65]. In essence, the direct HDS pathway includes the hydrogenation stage, and can called "direct" only arbitrarily.

Along with ethylbenzene, Geneste et al. [66] found dihydrobenzothiophene among products of the reaction of benzothiophene with ethylbenzene at elevated hydrogen pressure [66]. The authors suggested that the reaction involves consecutive formation of dihydrobenzothiophene and ethylbenzene. Kilanowski et al. [67] state that desulfurization of benzothiophene gives ethylbenzene as a single product. By contrast, with dibenzothiophene, a number of intermediate products were detected [15, p. 490]. The pseudo-first order rate constants of direct HDS is 2.8×10^{-5}, and the respective value for partial hydrogenation of the aromatic ring in dibenzothiophene is 4.2×10^{-8} m^3 kg^{-1} cat. s^{-1}.

Egorova and co-workers [68, 69] studied hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) on sulfidized NiMo/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3 catalysts. Some researchers explained the lower rate of 4,6-DMDBT desulfurization in terms of a weak adsorption ability of the catalyst surface [70]. Other authors explained this phenomenon by the steric hindrance posed by methyl groups [71]. Kabe et al. [72] found that the absorption equilibrium constants of 4-methyldibenzothiophene and 4,6-DMDBT are even higher than that for unsubstituted dibenzothiophene on the CoMo/Al_2O_3 catalyst.

Mills et al. found [73] that the "anchor" adsorption of thiophene (σ-adsorption) slightly strengthens the C–C bonds in the thiophene ring and strongly weakens the C–S bonds compared with free tiophene. These findings made the authors to conclude that the C–S bond is cleaved in the course of thiophene adsorption on the coordinately unsaturated site of the MoS_2 via the sulfur atom (σ adsorption). Vecchi et al. [74] established that the bond strength increases in the order 4,6-DMDBT < 4-methyldibenzothiophene < DBT < 2,8-DMDBT. This is fully consistent with the results in [71, 72].

DFT quantum-chemical computations of various conformations of dibenzothiophenes adsorbed on sulfide catalysts showed that stable dibenzothiophene and 4,6-DMDBT molecules radically differ in adsorption ability from smaller thiophene and benzothiophene molecules [75]. The main reason for this difference is that dibenzothiophenes comprise two aromatic rings, which makes π adsorption (planar) more probable compared with "anchor." It was shown that methyl groups, indeed, prevent perpendicular σ adsorption of 4,6-DMDBT but practically do not prevent planar π adsorption of this aromatic molecule.

Analysis of the mechanism of the hydro-desulfurization reactions of thiophene and its derivatives, which are the principal heteroatomic components of crude oil and their removal is critical in the production of high-purity diesel fuels, allows one to assess the contribution of hydrogenation stages and pathways. As shown above, even the "direct hydrodesulfurization" pathway includes hydrogenation stages [65]. As the molecule is complicated, i.e. in going to BT, DBT, and substituted DBT (especially 4,6-dialkyldibenzothiophene), the hydrogenation pathway and, probably, hydrogenation attendant in the "direct hydrodesulfurization" pathway take more and more significance.

Modification of Co(Ni)Mo/Al_2O_3 Catalysts

As shown by Topsoe and co-workers, a highly active type II phase can be obtained by sulfidation at high temperatures. However, this by no means the best way to prepare such structures since high-temperature treatment can result in catalyst coking and loss of important edge centers. Therefore, it is desirable to find an alternative approach to active catalysts, for example, via using supports like carbon, that weakly interact with the active phase, as well as via introducing additives or complex-forming agents [26].

Carbon has long been used as a support in research works. In spite of good results, such supports have never been used in commercial catalysts. The reason is that carbon catalysts are impossible to regenerate in a usual way, i.e. by oxidation.

One of the ways to increase the activity of hydropurification catalysts is to introduce in them inorganic modifiers [26, 76, 77]. A great number of modifying additives were suggested. The optimal contents of such additives in catalysts are normally determined empirically. The mechanism of promoter action is far from being understood and can be explored for each concrete additive.

Quite a common modifier is phosphorus [78]. The reasons for its promoter action still not fully understood, and the available evidence is controversial. Sun et al. [79] reported that the activity of the CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts in hydrodenitrogenation decreases but in HDS increases only slightly or decreases. The highest activity is observed at the phosphorus content 1 wt % [80] and is associated exclusively with change in the acidity of alumina on addition of phosphorus acid. Liu et al. [81] found that phosphorus favors formation strong and medium-strength acidic centers and enhances dispersity of the active phase. Boron is fairly frequently used as a modifier [82–84]. By contrast, Lewandowski and Sarbak [85] found that modifying with boron increases the acidity of catalysts but has no effect of their activity in hydrodesulfurization. Silicon was also used as a modifying additive [77, 86, 87]. The activity of NiMo/Al_2O_3 catalysts is enhanced by In [88], Sn [89–91], or ZnO [92] modifiers.

Activity–modifyer content plots very frequently pass through a maximum at a certain Mo/modifier ratio. For example, NiMo/Al_2O_3 catalysts containing 1.2 wt % of Ga proved more active in model HDS reactions than NiMo/Al_2O_3 [93]. The activity of thiophene in HDS on Co–MoS_2/B/Al_2O_3 catalysts [82] decreases if the boron content is higher than 0.6 wt % (Fig. 4).

There have been a number of publications [94–100] reported on the formation of heteropoly compounds (HPC) on the surface of catalysts like Co(Ni)Mo(W)/γ-Al_2O_3 in the presence of additives. Okamoto et al. [94] suggest formation of a heteropolyanion structure in phosphorus-doped NiMo/Al_2O_3 catalysts. During synthesis of Ti–Mo catalysts from ammonium paramolybdate and TiO_2, Ti–Mo heteropoly acids (HPA) are formed on the surface [96]. Heteropoly compounds also form on the surface of oxide carriers (TiO_2, SiO_2, Al_2O_3) doped with Mo or W [94, 101]. According to [97–100], molybdenum stabilizes on the surface of silicon oxide as HPC.

One of promising modifiers for hydropurification catalysts is vanadium [103, 104]. Analysis of the patent literature [105] shows that vanadium-containing catalysts are used for hydroprocessing of hydrocarbon raw materials. The catalytic activity of vanadium-modified aluminum–nickel–molybdenum (ANM) catalysts in hydropurification of diesel fractions was studied in detail [105–112]. The strongest effect on HDS and hydrogenating activity was observed when the concentration of V_2O_5 in the catalyst varied in the

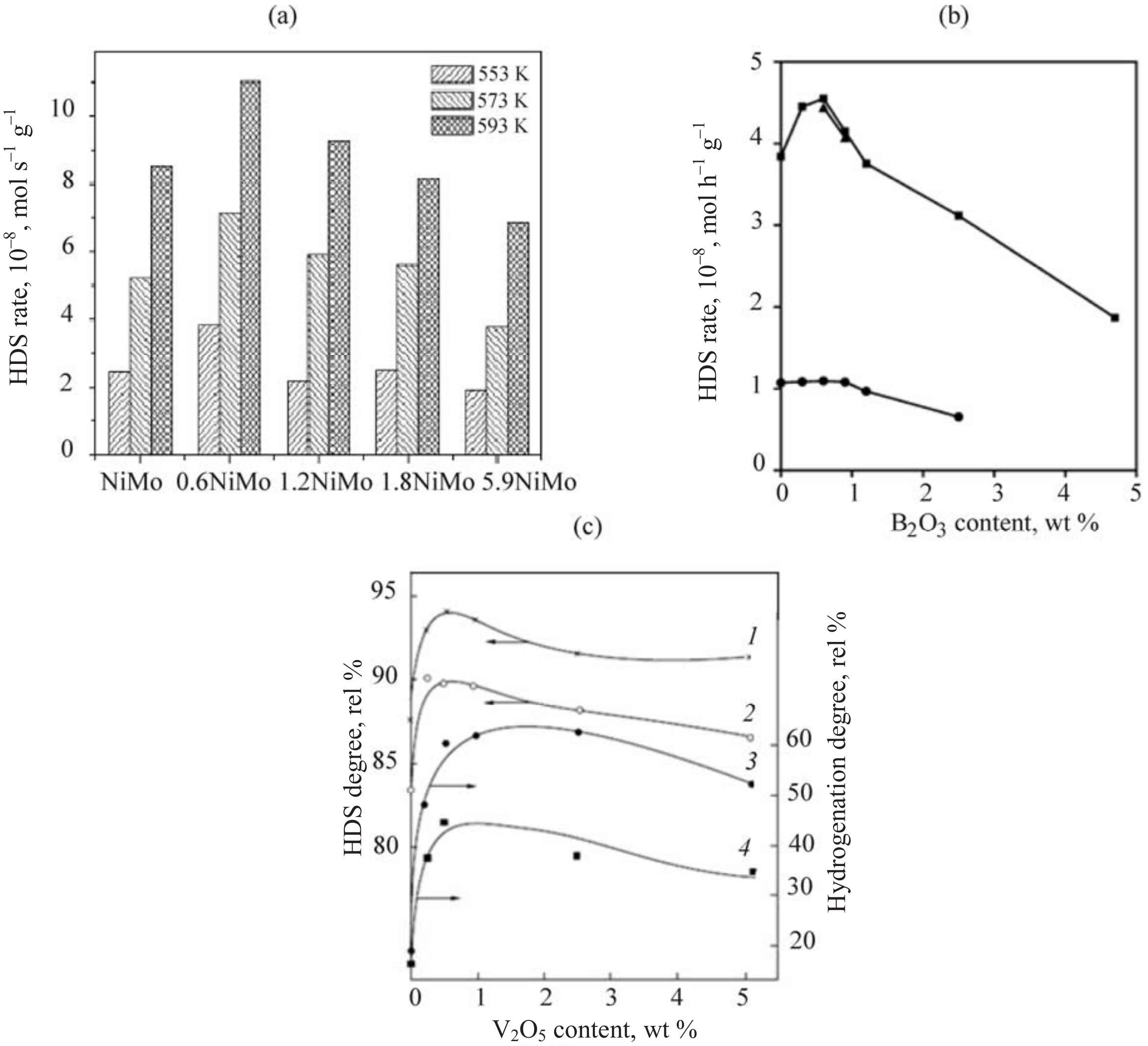

Fig. 4. Effect of (a) gallium, (b) boron, and (c) vanadium additives on the activity of hydrodesulfurization catalysts. (a) The *x* axis shows the content of Ga, wt %, in the nickel–molybdenum catalysis in the HDS of 4,6-dimethyldibenzothiophene [93]; (b) (●) $MoS_2/B/Al_2O_3$; (■) $Co/MoS_2/B/Al_2O_3$, double impregnation; (▲) $Co/MoS_2/B/Al_2O_3$, simultaneous impregnation [82]; and (c) $NiMoV/Al_2O_3$ catalysts with varied content of V_2O_5 [107].

range 0.25–1 wt %. The MoO_3/V_2O_5 molar ratio for the most active catalysts was about 12–13 (Fig. 4).

The character of the dependence of catalyst properties on vanadium content allows us to suggest that vanadium additives, too, form 12-series heteropoly compounds (hereinafter VMo_{12}). This suggestion fairly explains the results of observations on the catalytic activity and bond strength between active component and support.

To obtain evidence for the suggested formation of an active precursor of the sulfide phase, we synthesized a 12-series vanadium–molybdenum compound $(NH_4)_x[V(Mo_{12}O_{40})]\cdot nH_2O$ and used to to prepare an $NiMoV/Al_2O_3$ catalyst (Table 3, catalyst no. 3). For the sake of comparison we also prepared $NiMoV/Al_2O_3$ from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_4VO_3 (catalyst no. 2), as well as $NiMo/Al_2O_3$ (catalyst no. 1). The contents of MoO_3 and NiO in all the three catalysts were the same. The Mo:V ratio in catalysts nos. 2 and 3 was 12. The catalysts were tested in hydropurification of light coking gasoil. Table 3 lists the relative hydrosulfurizing and hydrogenating activities toward bi- and tricyclic aromatic hydrocarbons, which were calculated as the ratio of the HDS and hydrogenation degrees on catalysts nos. 2 and 3 to the respective value for catalyst no. 1 whose activity was taken to be 1 at all temperatures. The hydrosulfurizing

Table 3. Activities of catalyst nos. 2 and 3 relative to catalyst 1

Temperature, °C	HDS degree		Hydrogenation degree			
			Bicyclic aromatic hydrocarbons		Tricyclic aromatic hydrocarbons	
	catalyst no. 2	catalyst no. 3	catalyst no. 2	catalyst no. 3	catalyst no. 2	catalyst no. 3
340	1.2	1.4	1.1	1.9	1.2	1.7
360	1.1	1.3	1.4	2.3	1.1	1.5
390	1.1	1.2	1.2	1.6	1.2	1.3
410	1.0	1.1	1.1	1.4	0.9	1.1

and hydrogenating activities of catalyst no. 3 prepared from the heteropoly complex proved to the highest. The lowest activity was found to be characteristic of a vanadium-free catalyst. It was also established that vanadium additives are efficient only is there is the possibility that a MO–V compound forms during catalyst synthesis [111]. The compositions and methods of synthesis of vanadium-doped ANM catalysts for hydropurification of various types of oilstock are protected by inventor certificates and patents [113–115].

Obviously, the formation of molybdenum (and, probably, tungsten) HPC on introduction of most modifiers into hydropurification catalysts is a common reason for the enhanced activity of the latter. A hypothesis arises that the oxide precursor of active sulfide phases in all hydropurification catalysts like Co(Ni)Mo(W)/γ-Al_2O_3 (and on other oxides) contains Mo or W heteropoly compounds. These compounds form at the hydrothermal stage of catalyst synthesis when Mo(W) come into direct contact with a heteroatom. The role of the heteroatom (complex-forming agent) can be played by a support (Si, Al, Ti, etc.) or a modifier (any element of the Periodic Table) atom.

Application of HPC for Synthesis of Hydropurification Catalysts

The use of Mo and W heteropoly compounds opens up new perspectives for the synthesis of hydropurification catalysts. Into an HPC molecule one can incorporate simultaneously principal components (Mo or W) as ligands, promoters (Co or Ni) as outer-sphere cations or complex-forming agents, and modifiers (P, Si, In, B, V, Sn, Zn, Ga, etc.). This allows the support to be impregnated in one stage and thus radically facilitate the synthetic procedure. Most HPC are readily soluble, which makes it possible to synthesize hydropurification catalysts with high contents of active components. Therewith, the components are mixed at the molecular level, and their ratio and electronic state are rigidly controlled. When adsorbed on support surface, Mo and W heteropoly compounds preserve their regular structure [116]. Activity of Co(Ni)Mo(W)/Al_2O_3 catalysts on the basis of Mo and W heteropoly compounds with a Keggin structure was studied in [105, 110, 117–121].

Table 4 lists the relative HDS activities of these catalysts. The samples of NiMo/γ-Al_2O_3 catalysts differ from each other in the nature of the heteroatom in the molybdenum HPC used in their synthesis. The relative HDS activities of the other catalysts were estimated by dividing the HDS degree for a specific catalyst by the HDS degree for catalyst I-1 at every temperature. The most significant activity enhancement was observed with HPC containing vanadium as a complex-forming agent (I-5, VMo_{12}-HPC) or in the coordination sphere (I-4, $PVMo_{11}$-HPC).

The activity of catalysts on the basis molybdenum HPC with a Keggin structure, in the hydrogenation of PAH is shown in Fig. 5a. The strongest activity enhancement, like with HDS, is observed with samples I-4 and I-5. The catalyst on the basis of VMo_{12}-HPC exhibits a 1.5–2-fold higher hydrogennating activitity at 340–390°C than the reference sample (I-1).

Hydropurification catalysts with tungsten as an active component, rather than molybdenum, have not gained acceptance in industry. Therefore, we chose a mixed system containing nickel-promoted molybdenum and tungsten oxide on an alumina support. Characteristics of the NiMoW/Al_2O_3 catalysts (samples I-6, I-7, and I-8) are presented in Table 4.

Tungsten-doped samples are more active both in HDS and in hydrogenation over virtually the entire temperature range (Table 4, Fig. 5b). The results with

Table 4. Compositions and relative HDS activities of catalysts prepared on the basis of Keggin HPC

Catalyst no.	Mo or W compounds used for catalysts synthesis	Content, wt %				Content in catalyst after testing, wt %		Relative activity			
		MoO_3	WO_3	NiO	V_2O_5	coke	sulfur	340°C	360°C	390°C	410°C
I-1	APM[a] + Ni	11.2	–	2.4	–	3.00	1.55	1.00	1.00	1.00	1.00
I-2	$SiMo_{12}$-HPC + Ni	11.2	–	2.1	–	–	–	1.26	1.02	0.99	0.90
I-3	PMo_{12}-HPC + Ni	10.0	–	2.2	–	1.95	2.19	1.22	1.11	1.17	1.09
I-4	$PVMo_{11}$-HPC + Ni	10.7	–	2.5	0.49	1.70	2.54	1.35	1.27	1.28	1.06
I-5	VMo_{12}-HPC + Ni	11.3	–	2.2	0.41	–	–	1.41	1.28	1.19	1.09
I-6	APT[b] + APM + Ni	8.0	3.4	2.3	–	–	–	1.36	1.13	1.20	1.06
I-7	SiW_{12}-HPC + APM + Ni	8.0	3.5	2.2	–	–	–	1.40	1.15	1.25	1.08
I-8	PW_{12}-HPC + APM + Ni	8.0	3.1	2.4	–	–	–	1.57	1.38	1.21	1.09

[a] Here and hereinafter, APM is ammonium paramolybdate. [b] APT is ammonium paratungstate.

PAH hydrogenation are not so unambiguous. Tungsten additives, too, favor higher activity, but APT shows better results than SiW_{12}-HPC, whereas PW_{12}-HPC is more active at low temperatures only.

There are catalysts [92, 122, 123] and technologies for hydropurification of diesel fuel employing catalysts on the basis of SiW_{12} and $SiMo_{12}$ heteropoly compounds [124, 125] are protected by patents. In the mid-1980s a group of researchers from Samara State Technical University (SSTU) headed by Yu.V. Fomichev and A.N. Loginova developed an SiW_{12}-HPC-containing catalyst (GR-24M) for hydropurification of lube stock, which was used in industry.

There has been a systematic activity study of catalysts on the basis of Anderson heteropoly compounds [117, 118, 121]: $CrMo_6$, $MnMo_6$, $FeMo_6$, $CoMo_6$, $NiMo_6$, $CuMo_6$, $ZnMo_6$, and $GaMo_6$. The highest HDS activity was observed with catalysts on the basis of Ni heteropoly compounds, and those with Co, Cr, Zn, and Ga ranked slightly below (Fig. 6). The lowest activity was observed with catalysts on the basis of Mn and Cu heteropoly compounds. The

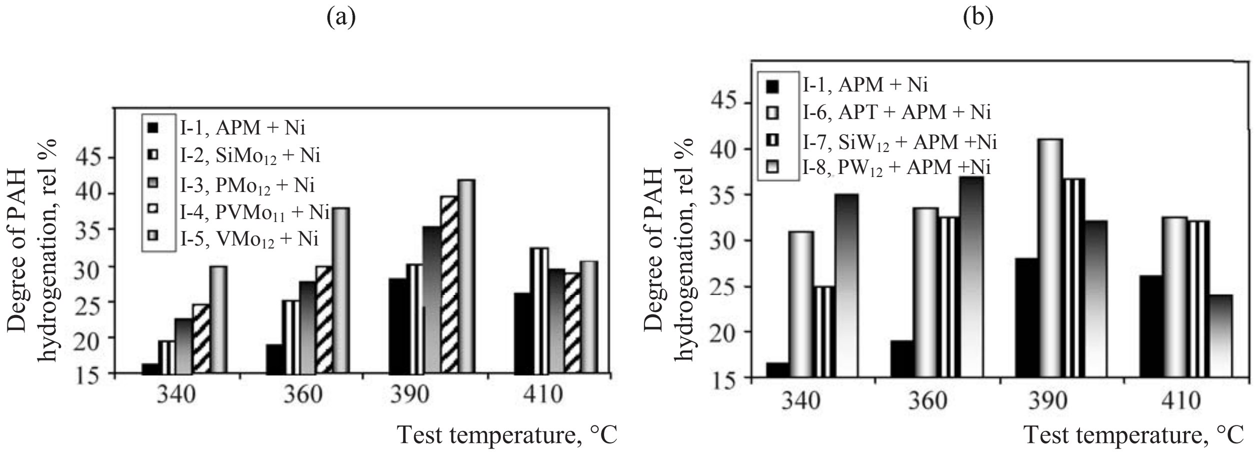

Fig. 5. Hydrogenating activity of catalysts vs. temperature. Catalyst: (a) molybdenum-doped and (b) tungsten-doped. For catalyst numbers, see Table 4.

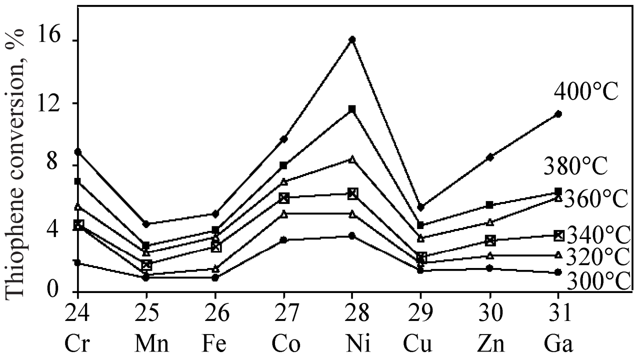

Fig. 6. Activity of $NiXMo_6(S)/\gamma\text{-}Al_2O_3$ catalysts in thiophene hydrogenolysis.

resulting curves can be interpreted in part by means of Chianelli calculations [36, 126, 127] which showed that the role of promoters is to increase or decrease the number of electrons on the antibonding orbital of Mo in the active mixed sulfide phase. An increase of the electron density on Mo should weaken the Mo–S bond in the active phase and decrease the energy of formation of active centers. This is indeed the case with Ni and Co. In the case of elements withdrawing electron density from Mo (for example, Cu), an opposite effect takes place, which has a negative impact on the catalytic activity.

CONCLUSION

Many questions in the problem of catalysis with transition metal sulfides can presently be considered answered. Analysis of the mechanisms of reactions of thiophene and its derivatives shows that the contribution of the hydrogenation stage increases with increasing complexity of the sulfur compound, i.e. in going from BT, DBT, and substituted DBT (especially 4,6-dialkyldibenzothiophenes). As known, hydrogenation plays an important role in hydrodenitrogenation. Of particular importance is hydrogenation of polyaromatic hydrocarbons.

The role of the Co–Mo–S phase is considered conclusively established. The issues under discussion are whether multilayer structures like Co–Mo–S are present, what is the role of defectless, so-called metal centers, and whether the Co(Ni) and Mo sulfide phase can be segregated. Effect of the orientation of Co–Mo–S monolayers on the support is under discussion.

Sulfidation at high temperatures can transform a type I phase into a highly active type II phase, but, according to H. Topsoe, this is not the best approach to type II structures. Therefore, it is desirable to find an alternative process for catalyst production, in particular, introduction of additives or complex-forming agents.

A hypothesis is being formed that the oxide precursors of active sulfide phases in all hydropurification catalysts like Co(Ni)Mo(W) on aluminum, silicon, titanium, or zirconium oxides contain Mo or W heteropoly compounds. The latter are formed at the hydrothermal stage of catalyst synthesis is there is direct contact of Mo(W) atoms, a heteroatom, and an acid medium. The role of complexing heteroatom can be played by a support (Si, Al, Ti, etc.) or a modifier (any element of the Periodic Table) atom. Apparently, the general reason for the enhancement of activity on introduction of modifiers into hydropurification catalysts consists in the formation of molybdenum HPC.

From this it follows that HPC are the best precursors of molybdenum (tungsten) oxides entering into the composition of catalysts. Using HPC in the synthesis of hydropurification catalysts opens up new possibilities. An HPC molecule can simultaneously comprise principal active components (Mo or W), promoters (Co or Ni), and modifiers (P, Si, In, B, V, Sn, Zn, Ga, etc.) as ligands, outer-sphere cations, or complex-forming agents. In its turn, this allows impregnation of the support to be performed in one stage, which radically facilitates the synthetic procedure. Most heteropoly acids and HPC are readily soluble, thus making it possible to synthesize hydropurification catalysts with high contents of active components. Therewith, the components are mixed at the molecular level, and their ratio and electronic state are rigidly controlled. Upon adsorption on the support surface Mo and W heteropoly compounds preserve their regular structure.

Even though many questions of sulfide catalysis have been studied in detail, there is still no complete picture of the genesis of catalysts during their preparation, impregnation, drying, calcination, and sulfidation, which is especially evident when HPC are used as precursors of active phases.

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