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CATALYTIC REACTION MECHANISMS

In Situ Radioisotopic Study of the Active Sites of Sulfide CoMo Catalysts and the Mechanism of Thiophene Hydrodesulfurization

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Abstract—The mechanism of thiophene hydrodesulfurization over sulfide catalysts for hydrotreating and the effect of the catalyst composition and feed on the number, distribution, and performance of active sites were studied using ^{35}S and ^{3}H isotopes. Based on the results of radioisotopic study, a method for systematic testing–monitoring of sulfide Co(Ni)Mo catalysts for hydrotreating is developed. The method involves the evaluation of the fraction of the active phase surface occupied by SH groups and the ratio between the concentrations of the surface SH groups and coordinatively unsaturated sites including functioning vacancies. General conditions for the formation and functioning of active sites are formulated on the basis of the monitoring data. Criteria for evaluation of the catalyst performance under conditions of hydrodesulfurization of various kinds of crude are proposed. The results of the pilot tests of commercial catalysts suggest that the criteria proposed are suitable.

INTRODUCTION

The practice of the last decades shows that oil refining needs more and more novel efficient catalysts for hydrotreating. This is due to the involvement of heavier oil fractions in the refining process and the toughening of environmental requirements for the products. Along with the problem of creating new catalysts for deep oil refining, the industry is facing the problem of developing and selecting catalysts for hydrotreating of oil narrow cuts and some fuels.

A practical application of the results of basic studies in catalysis by supported metal sulfides should be the formulation of criteria for the choice of starting compositions that should be the focus in developing new and improving existing commercial catalysts, as well as criteria for choosing among already developed catalytic systems that meet the requirements of a specific process and the nature of starting materials. Up to now these studies have concerned the structure of the catalyst and their active sites, which is the results of the development and use of modern physicochemical techniques and apparatus for surface studies and relative simplicity of interpreting their results.

Indeed, although many schemes of thiophene decomposition over sulfide catalysts have been proposed, there are no reliable experimental data that give priority to one of them. This is due to the lack of our understanding of the structure and performance of active sites of the sulfide catalysts. The role of sulfide sulfur in the hydrogenolysis of sulfur-containing compounds remains unclear. Structural models cannot answer these questions. The most important problems are as follows: are the active sites formed under conditions of catalysis and what is their relative amount? Specifically, it is commonly accepted nowadays that anionic vacancies play a key role in catalysis by transition metal sulfides [1–17]. Numerous models of active sites including anionic vacancies have been proposed [12]. Most of them are based on the assumption that catalytic transformations occur on coordinatively unsaturated sites (CUS), which can exist in the structure (e.g., on the corners and edges) of MoS_2 clusters or form in the course of preliminary reduction of a catalyst or a catalytic reaction. However, there are no experimental data that confirm the formation and functioning of vacancies in the course of a reaction. This is due to the fact that such information is difficult to obtain even using modern *in situ* experimental techniques. It is necessary to find an additional way to obtain unambiguously interpretable data on the dynamic properties of the system. Therefore, the use of isotopic tracer techniques in combination with other methods for catalyst studies can be very efficient because it allows an *in situ* study of the behavior of all components in the system, including both reactants and the catalyst, and gives dynamic information on the interaction of the active sites with reactant molecules.

The use of the radioactive isotope ^{35}S allowed us to reveal that in the hydrodesulfurization of organosulfur compounds, sulfide sulfur participates in hydrogen sulfide formation [18–21]. There may be two reasons for the transfer of the radioactive sulfur from the catalyst-^{35}S (Cat-^{35}S) to H_2S. First, the surface ^{35}SH groups of the catalyst may be involved in thiophene hydrogenol-

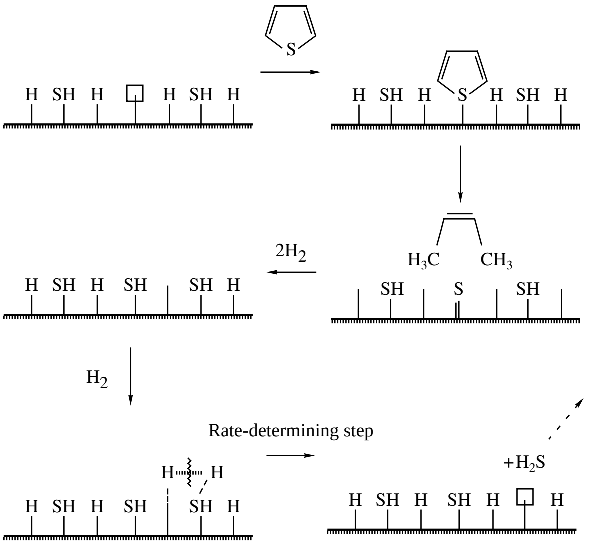

Fig. 1. Scheme of the "displacement" mechanism of thiophene conversion over the sulfide catalyst.

ysis to form radioactive H_2S and, second, it may be due to the isotope exchange between ^{35}SH groups of the catalyst and nonradioactive hydrogen sulfide formed in the course of thiophene hydrogenolysis. The authors of [21] did not find any correlation between the catalytic activities in the isotope exchange and thiophene hydrogenolysis, whereas such a correlation was found in [19, 20, 22–25]. The data obtained provide evidence on the important role of sulfide sulfur of the catalyst in hydrodesulfurization.

Deuterium was used as a tracer in most isotopic studies of the hydrodesulfurization mechanism [26–35]. Attempts were made to find a relationship between the H–D exchange, molecular hydrogen adsorption, and catalytic activity [26, 28–30] or to determine the source of hydrogen that participates in the hydrogenolysis of the C–S bond in thiophene: the thiophene molecule, catalyst, or the gas phase [27]. However, data on deuterium–hydrogen exchange without comparison with data on sulfide sulfur behavior did not allow the authors to draw a definitive conclusion on the reaction mechanism.

Taking this into account, we studied the mechanism of thiophene hydrodesulfurization using both ^{35}S [36, 37, 39–48] and ^{3}H [38, 40, 43, 46, 48]. We showed that during thiophene hydrodesulfurization, sulfur of the catalyst is replaced by sulfur of thiophene [36–40]. Data obtained using tritium proved that the appearance of radioactivity in the hydrogen sulfide that is formed in the hydrogenolysis of the organosulfur compound on the surface of the sulfide catalyst containing the ^{35}S tracer is due to the displacement of the labeled ^{35}S groups of the catalyst into the gas phase in the form of hydrogen sulfide and is not due to isotope exchange. These findings allowed us to propose [46, 48] the mechanism of thiophene transformation on the surface of the sulfide catalyst (Fig. 1). According to this mechanism, the anionic vacancies, SH groups, dissociatively (reversibly) adsorbed hydrogen, and molecular hydrogen are present on the surface of the active phase of the CoMo sulfide catalyst. The catalyst is characterized by a certain ratio between the number of vacancies and SH groups. The adsorption of thiophene (or other organosulfur compound) on the anionic vacancy changes this ratio, and the catalyst transforms into a metastable state. The hydrogenolysis of the C–S bond and the formation of the hydrocarbon fragment of the organosulfur compound involves the reversibly and dissociatively adsorbed hydrogen and is accompanied by the formation of a new SH group that is equivalent to the existing ones. The catalyst transformation from the metastable state is due to the elimination of one of the surface SH groups and the formation of a new vacancy. The SH group is removed by interaction with molecular hydrogen to form hydrogen sulfide. The rupture of the H–H bond is the slowest and rate-determining step of the whole reaction. However, some details of the mechanism of vacancy formation, the interaction of the SH group with molecular hydrogen, and the displacement of the excess SH group to the gas phase remain unclear. In particular, it is important to know or at least evaluate the ratio between the numbers of SH groups and vacancies and its possible variations depending on the catalyst composition and reaction conditions.

The goal of this work is to study systematically the effects of the catalyst composition, crude, and reaction conditions on the performance of the active sites; the evaluation of the ratio between the number of SH groups and vacancies, and the fraction of the surface unoccupied by the SH groups, and, on the basis of these data, to develop a method for predicting the catalyst efficiency in hydrodesulfurization processes.

EXPERIMENTAL

Catalysts

We used catalysts prepared by conventional impregnation of γ-Al_2O_3 (specific surface area, 212 m^2/g; pore volume, 0.8 cm^3/g; and average pore diameter, 124 Å) and silica gel ASK (specific surface area, 363 m^2/g; pore volume, 0.96 cm^3/g; and average pore diameter, 98 Å) with aqueous solutions of ammonium heptamolybdate and cobalt or nickel nitrates followed by drying and calcination at 400°C. For the preparation of CoNi catalysts, supports were impregnated with a mixed solution of $Ni(NO_3)_2$ and $Co(NO_3)_2$. After impregnation, the catalysts were dried in air for 24 h at room temperature and for 2 h at 110°C. The concentration of metals in the samples was varied from 1 to 25%.

Commercial catalysts used in pilot testing contained from 3 to 6% of CoO and from 12 to 20% of MoO_3. Alumina was used as a support for all the catalysts. The model catalysts containing active metal oxides in the range of concentrations from 0 to 24% MoO_3 and from

0 to 12% CoO were prepared for the radioisotope testing. The catalysts for radioisotope testing were sulfided with a 5% H_2S/H_2 gas mixture for 4 h.

The pore structure of the catalysts was determined by mercury porosimetry on a Cultronix automatic porosimeter. X-Ray diffraction analysis of the supports and catalysts was carried out on a DRON-2 diffractometer. The degree of metal reduction was measured by the volumetric method, and their concentrations in the catalysts were determined by atomic absorption spectroscopy.

Radioactive Substances

A sample of elemental sulfur labeled with the ^{35}S radioisotope was prepared by recrystallization from toluene of tracer amounts of sulfur ^{35}S (Amersham Pharmacia Biotech) with non-radioactive elemental sulfur. The molar radioactivity (MR) of the sample was 1.2–2.0 GBq/mol. Hydrogen sulfide $H_2{}^{35}S$ was prepared by sulfiding the catalyst with sulfur ^{35}S. The MR of thiophene-^{35}S (VO Isotope) was 1.3 GBq/mol.

Sulfiding of Catalysts

Sulfiding with elemental sulfur ^{35}S was carried out in an autoclave with a volume of 21 cm^3 under a hydrogen pressure of 60 atm at 360°C and a weight catalyst : sulfur ratio of 5 : 1 or in the reactor of the experimental setup with a 5% $H_2{}^{35}S/H_2$ mixture at 0.5–1.0 atm or with thiophene-^{35}S.

Sulfiding with thiophene-^{35}S was carried out by introducing 3-μl thiophene pulses into the reactor at 360°C followed by the chromatographic analysis of the products. After the steady-state regime of the H_2S formation was reached, the feeding of the thiophene-^{35}S pulses was stopped.

Radioisotope Testing

The sulfide catalyst containing radioactive sulfur was loaded in the reactor of an experimental pulse microcatalytic setup combined with a radiochromatograph. The weighed portion of the catalyst was 100 mg. After the catalyst was treated in a He flow, the reactor was fed with hydrogen, which also served as a carrier gas for the radiochromatograph. The pulses of unlabelled thiophene of a 1-μl volume were successively supplied to the catalyst.

The signals of the thermal conductivity detector of the chromatograph and a flow counter of radioactivity were processed in the on-line regime with the Multichrom 2.74 program. The concentrations of hydrocarbons C_4, hydrogen sulfide, and unreacted thiophene, as well as MR of H_2S were measured at the outlet of the reactor. The radioactivity was found only in hydrogen sulfide. As new portions of unlabelled thiophene were introduced into the reactor, the MR of the hydrogen sulfide gradually decreased because of the displacement of the radioactive sulfur of the catalyst by the nonradioactive sulfur of thiophene.

The radioactivity of hydrogen sulfide was measured with a flow proportional counter connected to a multichannel analyzer of a Protoka (Russia) or a ROBOTRON (GDR) instrument.

The amount of sulfur in the catalyst samples was estimated by measuring the specific radioactivity (SR) of Cat-^{35}S and comparing this value with that of sulfur of the sulfiding agent.

Mathematical Processing of Experimental Results

The plots of hydrogen sulfide MR vs. the amount of reacted thiophene were approximated by exponential curves (Eq. (1)). The exponential form of the equations is due to the fact that the isotope exchange and substitution processes are described by the first order equations. Curves were approximated using the CurveExpert 1.34 program by the self-consistency method up to the satisfactory convergence of results in successive iterations. As a rule, the number of iterations was 35–40, the standard error of approximation was 1–2%, and the correlation coefficient was at least 0.997.

$$\alpha = \sum_{i=1}^{n} A_i \exp(-\lambda_i x). \tag{1}$$

Equation (1) is the superposition of exponential terms each describing the processes of isotope substitution of various intensities that occur simultaneously on various catalyst active sites differing in the reactivity. For the unpromoted Mo catalyst, Eq. (1) has a monoexponential form. Biexponential Eq. (1) is typical of a bimetallic catalyst, usually Co(Ni)–Mo(W). The preexponential factor A_i determines the fraction of thiophene molecules reacted on the sites of this type. When the sites of only one type are present ($i = 1$), then A_i = 100%.

The integration of Eq. (1) allows one to estimate the amount of sulfur in the catalyst that is capable of forming hydrogen sulfide on the sites of this type:

$$S_i = \frac{32}{22.4 \times 100} \int_0^{\infty} A_i \exp(-\lambda_i x)\,dx. \tag{2}$$

After integration of Eq. (2) we obtain

$$S_i = \frac{32}{22.4 \times 100} \frac{A_i}{\lambda_i}. \tag{3}$$

When the curve is described by more than one exponent, that is, when the active sites of more than one type responsible for hydrogen sulfide formation are present on the surface, the total amount of mobile sulfur is the sum

$$S_{\text{mob}} = S_1 + S_2 + \dots. \tag{4}$$

If the thiophene conversion is known, it becomes possible to estimate the number of its molecules converted on the active sites of a given type for the time of passing (~3 s) of one 1 μl pulse through the catalyst, that is, the ratio of the number of thiophene molecules to the number of SH groups of this type. Hence, it is possible to determine how many molecules of hydrogen sulfide are formed with participation of one SH group under the experimental conditions, that is, the productivity of the active sites of this type:

$$P_i = \frac{\gamma_i}{100}\frac{A_i}{100}\frac{N_\mathrm{T}}{N_\mathrm{S}}. \tag{5}$$

Then,

$$P_i = \frac{\gamma}{100}\frac{A_i}{100}\frac{\nu\rho}{M_\mathrm{T}}/\frac{S_i}{M_\mathrm{S}}. \tag{6}$$

After substitution of Eq. (3) into Eq. (6) and a series of simple transformations, we obtain

$$P_i = 2.84\times10^{-3}\gamma\lambda_i. \tag{7}$$

Here M_S is the atomic weight of sulfur; M_T is the molecular weight of thiophene; $N_\mathrm{T} = \nu\rho/M_\mathrm{T}$ is the number of mmoles of thiophene in a pulse; $N_\mathrm{S} = S_i/M_\mathrm{S}$ is the number of mmoles of mobile sulfur (SH groups) of this type; P_i is the productivity of the active site of this type; S_i is the amount of mobile sulfur of this type (mg); x is the amount of H_2S formed in the course thiophene hydrodesulfurization (cm^3); α is the molar radioactivity of H_2S normalized to 100% with respect to the initial radioactivity (%); γ is the thiophene conversion (%); v is the volume of thiophene in a pulse (1 μl); ρ is the thiophene density (1.064 g/ml); and λ_i is the exponential factor.

Thus, when we know only the thiophene conversion and the exponent value in the equation describing a change in the molar radioactivity of hydrogen sulfide, we can estimate the productivity of the active site of each type.

Hydrotreating of Residual Oil

Residual oil from West-Siberian oil contained asphaltenes, 4.3%; S, 2.3%; N, 760 ppm; V, 40 g/t; and Ni, 60 g/t. The catalytic activity (50 g of catalyst) was determined in the course of RO hydrotreating in an autoclave (250 cm^3) at a temperature of 380°C and an H_2 pressure of 5 MPa for 5 h. Coke deposition on the catalyst was measured using a Q-1500 D DTA instrument (Hungary).

Pilot Testing

Ten commercial $CoMo/Al_2O_3$ catalysts were tested under pilot conditions in the hydrotreating of straight-run gasoline (120–180°C, sulfur concentration, 0.25 wt %) and diesel fraction (270–360°C, sulfur concentration, 1.24 wt %). A fixed-bed reactor contained 50 g of the catalyst. Preliminary sulfiding was carried out with a 3% H_2S/H_2 mixture for 18 h. The duration of each test was 180 h; pressure, temperature, and feed space velocity (6 MPa, 360°C, and 5 h^{-1}, respectively) remained constant during the whole run.

RESULTS AND DISCUSSION

1. Effect of Catalyst Composition on the Distribution and Functioning of Active Sites of Sulfide CoMo Catalysts

To monitor a change in the concentration of sulfide sulfur in the catalysts after sulfiding and during the reaction, helium was passed through the reactor for 30 min at 360°C. Then, several samples were treated with hydrogen for 7–8 min at the same temperature. The duration of hydrogen treatment was chosen to allow the duration of each radiochromatographic analysis during the radioisotopic testing of the catalysts to be 6–8 min, which corresponded to the interval between two successive thiophene pulses. Preliminary experiments showed that under reaction conditions a fraction of sulfide sulfur is removed from the catalyst surface for the first 5–6 min of hydrogen treatment and the duration of treatment does not result in a substantial change in the amount of sulfur in the catalyst. Table 1 compares the resulting data with the maximally possible stoichiometric sulfur concentration.

As can be seen from Table 1, after thermal treatment in a helium flow, all the samples contained sulfide sulfur in an amount close to stoichiometric. Hence, virtually complete sulfiding of all catalysts was reached under the chosen conditions irrespective of their composition. After treatment with hydrogen, the catalysts contained much less sulfur than before this operation. This means that a portion of the sulfide sulfur was converted to hydrogen sulfide during the first minutes of catalyst treatment with hydrogen. As a result, vacancies, which are necessary for the adsorption of organosulfur compounds during hydrodesulfurization, were formed on the surface of the active phase.

Changes in the molar radioactivity of hydrogen sulfide (α) during thiophene hydrogenolysis over unpromoted Mo catalysts are described by monoexponential equations (see Table 2). This is evidence for the fact that the SH groups on the surface of these samples are close to each other in reactivity (mobility); that is, these catalysts possess only one type of the active sites responsible for the rupture of the C–S bond. Analysis of data presented in Table 1 shows that with an increase in the Mo concentration in unpromoted Mo/Al_2O_3 catalysts, the fraction of mobile sulfur in the overall sulfide sulfur content somewhat decreases. Since mobile sulfur (SH groups) is located on the surface of MoS_2 clusters, this decrease is probably due to some decrease in the dispersion of the active phase of the catalysts caused by an increase in the size of MoS_2 clusters. It is important that an increase in the Mo concentration does not sig-

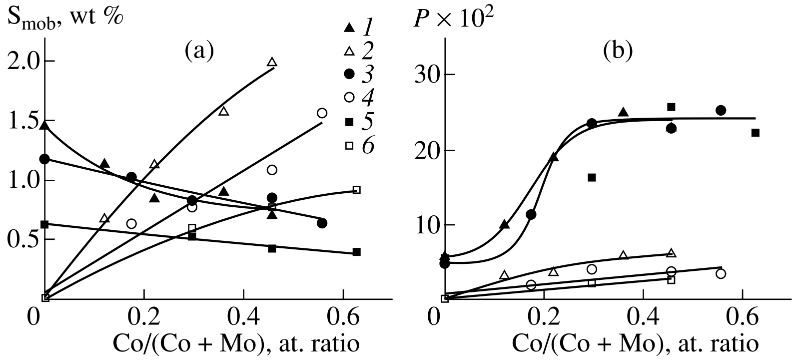

Fig. 2. (a) Amount of mobile sulfur and (b) productivity of the active sites vs. promoter concentration in the catalysts with the Mo concentrations (*1*, *2*) 12, (*3*, *4*) 8, and (*5*, *6*) 4%. Dark symbols refer to rapid sites and light symbols refer to slow sites.

nificantly change the productivity of active sites; that is, the nature of active sites in the Mo catalysts remains unchanged in the range from 2 to 12% Mo.

Changes in the MR of H_2S formed over the Mo catalysts containing Co are described by biexponential equations (Table 2). This points to the existence of SH groups of two types, which differ in reactivity toward H_2S formation (mobility), and, accordingly, active sites of two types on the surface of the active phase of these catalysts. We conditionally attribute the active sites of the unpromoted Mo catalysts to the “rapid” sites because the exponent values in the corresponding equations are close to the rapid components in the equations obtained for the promoted catalysts. These data completely coincide with the data published earlier for the limited number of samples [41, 42, 46], indicating the reproducibility of the results.

When the fraction of a promoter in the active phase of the catalyst increases, the amount of rapid sulfur decreases and the amount of slow sulfur increases. This is true for all the samples under study with the Mo concentration ranging from 4 to 12% (Fig. 2a). We previously observed the same pattern for the NiMo catalysts supported on alumina and activated carbon [42]. A

Table 1. Data on the radioisotopic testing of the hydrotreating catalysts Cat-^{35}S in thiophene hydrodesulfurization

Composition of active phase		*r*	ϒ, %	S_{stoich}, %	S_{He}, %	S_{H_2tot}, %	S_{mob}, %	S_{rapid}, %	S_{slow}, %	$P_{slow} \times 10^2$	$P_{rapid} \times 10^2$	CUS/SH
Mo, wt %	Co, wt %											
2	0	0	4.6	1.33	1.30	0.86	0.41	0.40	0	4.6	0	1 : 3.15
4	0	0	8.5	2.62	2.62	1.66	0.63	0.63	0	5.5	0	1 : 1.44
4	1	0.296	23.7	3.23	3.19	2.18	1.11	0.52	0.58	16.2	2.0	1 : 6.16
4	2	0.457	30.6	3.79	3.66	2.43	1.16	0.41	0.74	25.7	2.5	1 : 3.31
4	4	0.628	18.6	4.91	4.85	3.24	1.29	0.38	0.92	22.1	3.5	1 : 2.04
8	0	0	14.3	5.33	4.81	3.38	1.20	1.18	0	4.9	0	1 : 1.24
8	1	0.174	31.6	5.89	5.77	3.81	1.65	1.02	0.64	11.4	1.9	1 : 2.38
8	2	0.296	55.6	6.46	6.44	4.12	1.60	0.83	0.77	23.5	3.9	1 : 1.65
8	4	0.457	57.4	7.59	7.44	4.97	1.92	0.84	1.09	22.8	3.7	1 : 1.82
8	6	0.558	52.1	8.70	8.52	5.63	2.18	0.63	1.54	25.2	3.4	1 : 1.73
12	0	0	19.7	8.00	7.27	5.10	1.44	1.44	0	5.5	0	1 : 0.82
12	1	0.120	32.7	8.56	8.45	5.75	1.79	1.13	0.68	9.9	3.1	1 : 1.12
12	2	0.219	48.7	9.12	9.00	5.72	1.96	0.84	1.13	18.8	3.5	1 : 1.19
12	4	0.360	75.8	10.25	10.11	6.62	2.45	0.89	1.56	24.8	5.6	1 : 1.51
12	6	0.457	67.9	11.37	11.22	7.08	2.66	0.69	1.97	22.9	6.0	1 : 1.44

Note: Reaction conditions: 100 mg of catalysts, H_2 flow rate 20 ml/min, T = 360°C, thiophene pulse 1 μl. $r = \frac{\mathrm{Co}}{\mathrm{Co + Mo}}$, at. ratio, the approximate contact time was 3 s.

decrease in the amount of rapid sulfur is likely due to the partial blocking of SH groups bound to Mo by the Co(Ni) sulfide particles formed in the promoted catalysts. Simultaneously, the number of slow SH groups bound to Co increases. The productivity of the active sites of both types increases with an increase in the Co concentration (Fig. 2b). The productivity of the slow sites increases monotonically and slowly, whereas the productivity of the rapid sites vs. the Co concentration is described by an S-shaped curve; when the degree of promotion r = Co/(Co + Mo) is higher than 0.3, the increase slows down and the curves level out onto a plateau.

We attempted to estimate the ratio between the concentrations of the surface SH groups, anionic vacancies, and the fraction of catalyst surface containing no SH groups (the latter was attributed to total CUS). The maximal amount of mobile sulfur on the catalyst (S_{mob}) is ~40% of stoichiometry [36–42]. Data on the correlation between the degree of reduction of the MoS_2/Al_2O_3 catalyst and its activity in thiophene hydrodesulfurization [49–56] confirm this suggestion. Of course, such an assumption is approximate, but it can be used to estimate the relative change in the ratio between the concentrations of SH groups and CUSs as a function of the catalyst composition and the treatment and reaction conditions. The number of CUS should be equal to a difference between the maximal possible number of SH groups of the catalyst and the detectable number, which corresponds to the S_{mob} value; that is, $\Sigma\text{CUS} = 0.4S_{stoich} - S_{mob}$.

We mean here that vacancies (V) are CUSs that directly participate in the reaction, that is, those sites on which thiophene molecules are adsorbed. The other CUSs were called unoccupied, or empty (“empty sites”, ES). We suggest that these sites are the centers of the reversible dissociative and molecular hydrogen adsorption. Thus, $\Sigma\text{CUS} = \Sigma\text{V} + \Sigma\text{ES}$.

Since the surface SH groups in the promoted catalysts are not uniform and differ in their reactivity (or “mobility”) as rapid and slow, then the anionic vacancies should also be divided into those associated with the rapid (V_{rapid}) and slow (V_{slow}) SH groups. According to the “displacement” mechanism of hydrodesulfurization (Fig. 1), one site for thiophene adsorption (one functioning vacancy) corresponds to one SH group participating in the H_2S formation. The involvement of the rapid or slow SH group in H_2S formation is not a random process and is determined by the site of the thiophene adsorption on the catalyst surface. Therefore, when thiophene adsorbs on V_{rapid}, hydrogen sulfide is formed with the participation of the rapid SH group. When thiophene adsorbs on V_{slow}, the process involves the slow SH group. The total number of vacancies is equal to the sum of slow and rapid vacancies: $\Sigma\text{V} = \Sigma V_{rapid} + \Sigma V_{slow}$.

The number of functioning vacancies V_i can readily be determined from the productivity P_i of the active site

Table 2. Equations for the change in the molar radioactivity (α, %) of hydrogen sulfide during thiophene hydrogenolysis over the CoMo $^{35}S/Al_2O_3$ catalysts with various compositions (for reaction conditions see Table 1)

Composition of active phase		$\frac{Co}{Co + Mo}$	Equation
Mo, wt %	Co, wt %		
2	0	0	$\alpha = 100\exp(-3.53x)$
4	0	0	$\alpha = 100\exp(-2.27x)$
4	1	0.296	$\alpha = 87.73\exp(-2.41x) + 12.27\exp(-0.30x)$
4	2	0.457	$\alpha = 84.93\exp(-2.96x) + 15.07\exp(-0.29x)$
4	4	0.628	$\alpha = 72.35\exp(-2.72x) + 27.65\exp(-0.43x)$
8	0	0	$\alpha = 100\exp(-1.21x)$
8	1	0.174	$\alpha = 90.66\exp(-1.27x) + 9.336\exp(-0.21x)$
8	2	0.296	$\alpha = 86.52\exp(-1.49x) + 13.48\exp(-0.25x)$
8	4	0.457	$\alpha = 82.38\exp(-1.40x) + 17.62\exp(-0.23x)$
8	6	0.558	$\alpha = 75.15\exp(-1.70x) + 24.85\exp(-0.23x)$
12	0	0	$\alpha = 100\exp(-0.99x)$
12	1	0.120	$\alpha = 84.34\exp(-1.07x) + 15.66\exp(-0.33x)$
12	2	0.219	$\alpha = 80.24\exp(-1.36x) + 19.76\exp(-0.25x)$
12	4	0.360	$\alpha = 71.61\exp(-1.15x) + 28.39\exp(-0.26x)$
12	6	0.457	$\alpha = 57.25\exp(-1.19x) + 42.75\exp(-0.31x)$

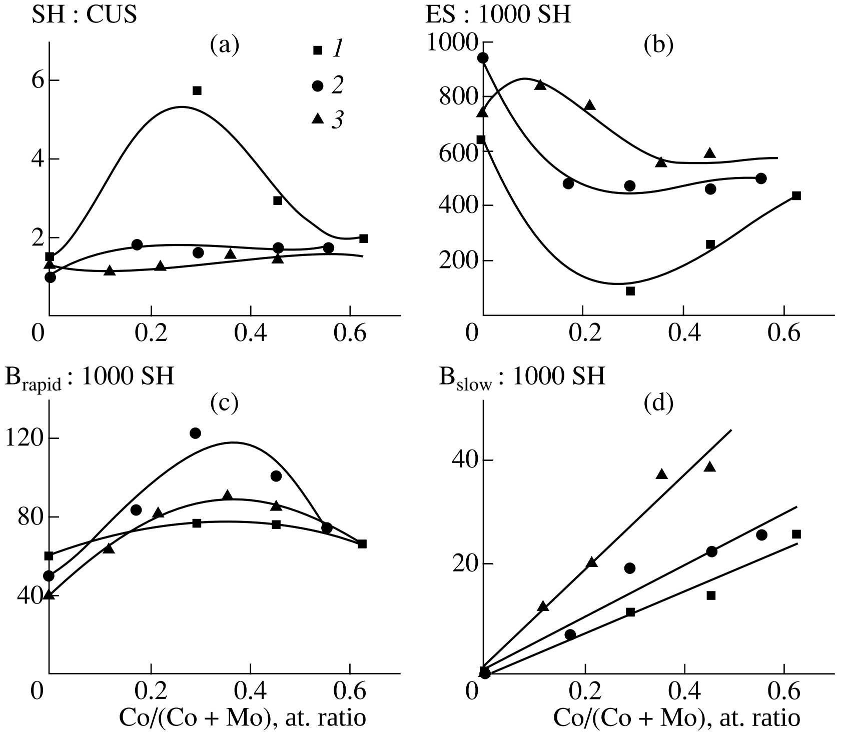

Fig. 3. Calculated dependences for (a) SH : CUS, (b) ES : 1000 SH, (c) V_{rapid} : 1000 SH, and (d) V_{slow} : 1000 SH on the degree of promotion for CoMo/Al_2O_3 catalysts containing (*1*) 4, (*2*) 8, and (*3*) 12% Mo. For experimental conditions see Table 1.

i. If P_i is the number of H_2S molecules formed on one SH group of the *i* type, then the reciprocal P_i^{-1} is the number of SH groups of the *i* type, one of which participates in the formation of one H_2S molecule. Since the number of H_2S molecules formed on the *i* sites is equal to the number of the functioning vacancies V_i, then P_i^{-1} corresponds to the ratio of the number of SH groups of the *i* type to the number of the functioning vacancies V_i of this type.

As follows from Table 1, an increase in the Mo concentration in the unpromoted Mo catalysts from 2 to 4% is accompanied by a significant growth of the fraction of the surface of the active phase containing no SH groups, and the SH : CUS ratio drops. A further increase in the Mo concentration results in a slower change in this ratio. When the S_{mob}/S_{tot} ratio (surface SH groups to the total amount of sulfide sulfur) decreases by ~20% with an increase in the Mo concentration from 2 to 4%, the SH : CUS ratio decreases 2.5 times. We concluded that, in the region of small Mo concentrations, not only the dispersion of the active phase but also its structure qualitatively changes with an increase in the metal concentration. The fraction of the functioning active sites (vacancies) per 1000 SH groups increases when the Mo concentration increases from 2 to 4% and then decreases. Changes in the V_i : 1000 SH ratio are 30–35 rel. %; that is, at a Mo concentration of 4%, thiophene is most often adsorbed on the active sites. In the range of lower Mo concentrations, thiophene adsorption on the sites is low because of the small concentration of sites. In the range of high Mo concentrations, adsorption decreases because of excess CUSs. The productivity of the active sites is virtually independent of the Mo concentration in the active phase. This means that at a Mo concentration higher than 4% thiophene hydrogenolysis is determined by the mobility of SH groups rather than by thiophene adsorption on the active sites.

The effect of the promoter concentration on the distribution of SH groups and vacancies is shown in Fig. 3 for the catalysts containing 4, 8, and 12% Mo. The introduction of even a small amount of Co (1%) in the 4% Mo catalyst sharply increases the fraction of the active phase surface occupied by SH groups (Fig. 3a). The maximal SH : CUS ratio for the 4% Mo catalyst corresponds to $r = 0.3$. With a further increase in the Co concentration in this catalyst, the fraction of the surface without SH groups decreased to the values typical of other samples. We suggest that the CoMoS phase formed in the low-percentage Mo catalyst is characterized by the highest density of SH groups and the lowest density of ESs (Fig. 3b). The coverage of the active phase with SH groups in the catalysts with higher Mo concentrations weakly depends on the promoter concentration.

As can be seen from Fig. 3c, the plots of the relative numbers of the vacancies connected with the rapid SH

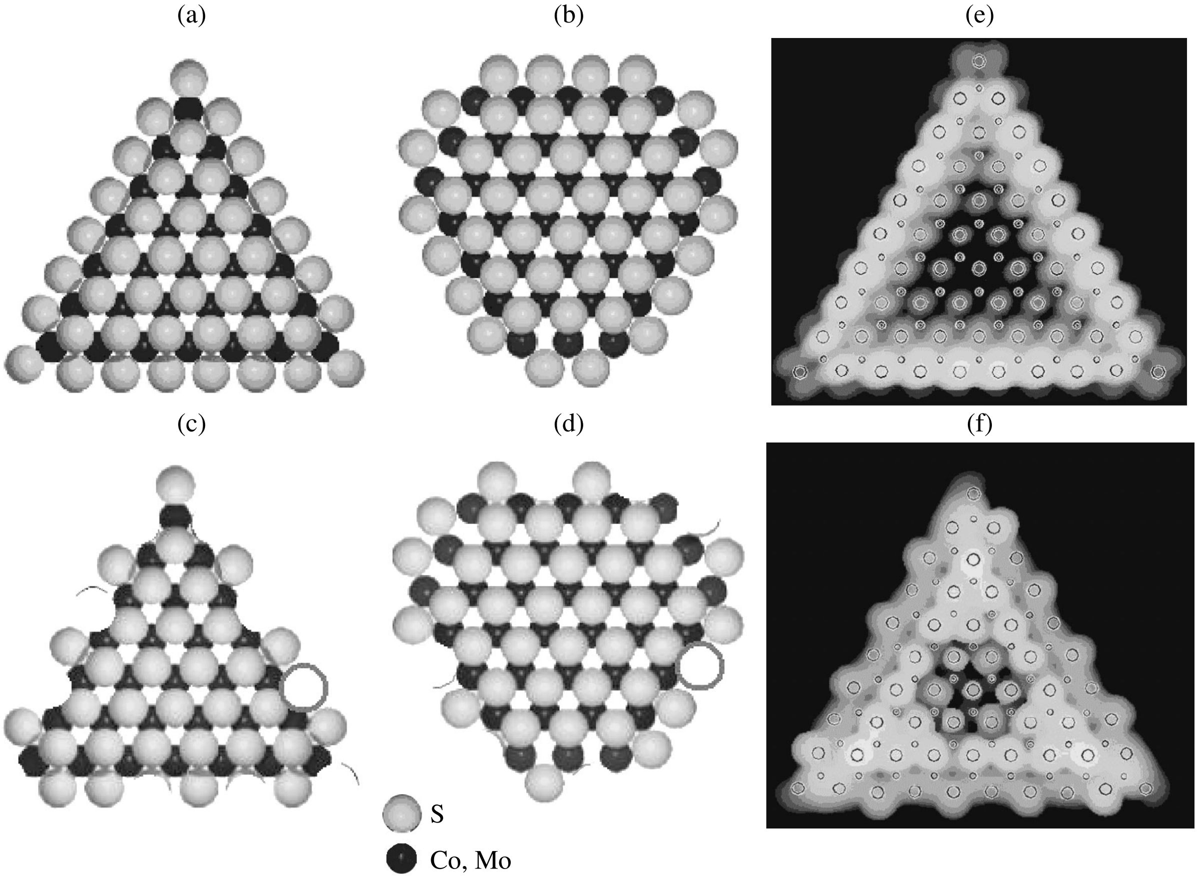

Fig. 4. Models of MoS_2 and CoMoS clusters (a, b) sulfided completely, according to the data of [57, 58], (e) according to [59]; (c, d) partially reduced under the reaction conditions, according to the data of radioisotopic testing, (f) according to [59]. The Co atoms in (b) and (d) are arranged along short ($\bar{1}010$) edges and the Mo atoms are arranged along $10\bar{1}0$ long edges.

groups vs. the Co concentration pass through a maximum. This is true for both low-percentage and high-percentage Mo-containing catalysts. The maximum on the curve for the 8% Mo catalyst is most pronounced and that on the curve for the 4% Mo catalyst is least noticeable. The maxima on all three curves are within the range $(0.3–0.4)r$ typical of the CoMoS phase formation. A further increase in the Co concentration leads to a decrease in the relative number of V_{rapid}, which is probably due to the formation of the Co_9S_8 phase. In this phase, the vacancies of this type are absent because rapid SH groups, which are related to V_{rapid} vacancies, are not formed on this surface. At the same time, the relative amount of vacancies V_{slow} belonging to the slow SH groups grows with an increase in the Co concentration in the active phase of the catalyst (Fig. 3d).

The SH : CUS ratios determined by radioisotopic testing are in good agreement with scanning tunnel microscopy (STM) data [57, 58] and findings obtained by modeling of the active phase of the catalyst by density functional theory [59]. This conclusion follows from the comparison of our calculations with the models of the unpromoted (Fig. 4a) and cobalt-promoted (Fig. 4b) MoS_2 clusters obtained by STM. The number of Mo atoms in the cluster model of molybdenum sulfide is 28, and that of terminal sulfur is 21. This size of the cluster corresponds to the Mo concentration in the catalyst of 8–12%. According to our data (Table 1), the SH : CUS ratio in the catalyst after its partial reduction, that is, under the reaction conditions, should be 1 : (0.8/1.3) or approximately 1 : 1. The number of Mo atoms in the model of cobalt-promoted CoMoS nanocluster was 27, that of Co atoms was 9, and that of terminal sulfur atoms was 18. The degree of promotion of this catalyst is $r = Co/(Co + Mo) = 0.25$, that is, the CUS : SH ratio in the catalyst partially reduced during the reaction should be approximately 1 : 1.5. Comparison of the image of the unpromoted partially reduced MoS_2 nanocluster obtained taking into account the calculated CUS : SH ratios (Fig. 4c) with the image of the similar cluster obtained by the modeling of the STM image with the density functional theory calculations (Fig. 4f) confirms the correctness of the above evaluation.

Note that, unlike the findings published previously and obtained under either ideal conditions of STM

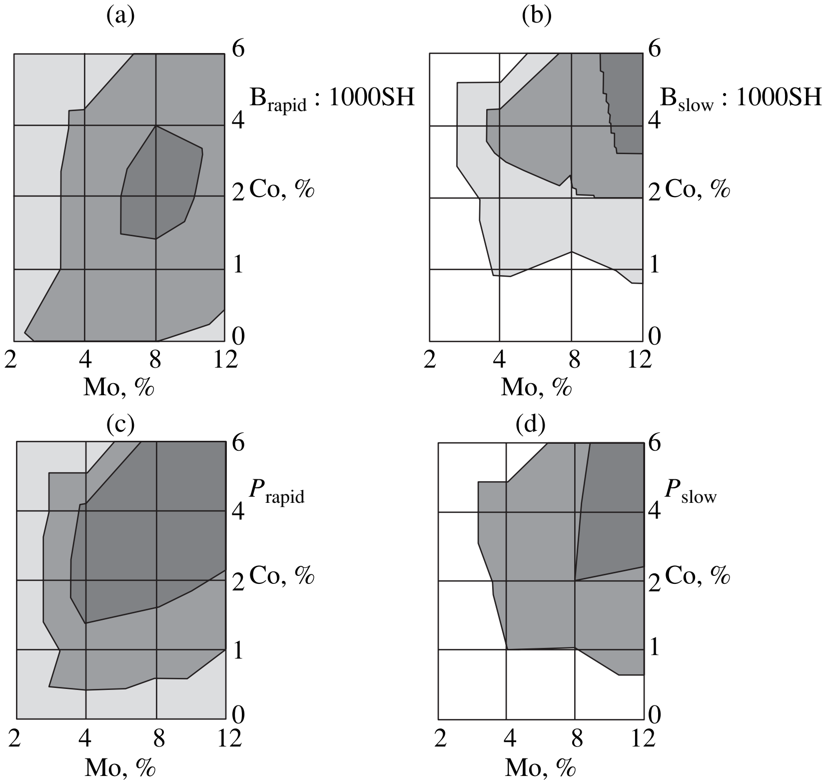

Fig. 5. Contour diagrams for (a, b) the distribution of functioning vacancies and (c, d) the productivity of active sites vs. the composition of the active phase in the CoMo/Al_2O_3 catalyst. The darkness of sections correlates with the parameter value.

(high vacuum, special gold carrier, and special method of deposition) or by theoretical calculations (all the literature data concern only MoS_2), our evaluations are based on *in situ* experimental data for both unpromoted MoS_2 and promoted CoMoS catalysts with different concentrations of the active components.

Variation in the density of functioning vacancies as a function of the catalyst composition for the rapid and slow sites is shown in a contour diagram (Figs. 5a, 5b). For comparison, the distribution of the productivities P_{rapid} and P_{slow} is presented in the same figure. It follows from the comparison of the diagrams in Figs. 5a and 5c that, although the region of distribution of rapid SH groups with the high productivity is broad and typical of all the catalysts containing more than 4% Mo and 1.5–2.0% Co, the region of the most dense location of vacancies V_{rapid} is markedly smaller and is limited to 10–11% Mo and 3–4% Co. Hence, the composition of the catalysts containing the most active rapid sites is limited to the region of the distribution of V_{rapid}. The productivity of slow sites and the concentration of vacancies monotonically increase with an increase in the Co and Mo concentrations. However, the region of the most efficient performance of these sites is determined by the location of vacancies. It is obvious that the regions of the highest productivities of rapid and slow SH groups partially overlap, whereas the regions with the most dense vacancies V_{rapid} and V_{slow} do not overlap. Therefore, the question arises as to how the regions of the highest activities of the sites of different types can be combined in one catalyst and whether this is necessary. We believe that the answer to this question is determined by the purpose of using the catalyst. That is, when it is necessary to hydrodesulfurize small molecules, the catalysts with the highest activity of rapid sites will be preferred. In this case, the catalyst composition will be determined by the conditions that are optimal for these sites; for example, it is the region of Co and Mo concentrations in which the highest concentration of the V_{rapid} vacancies is within the range $0.25 \leq r \leq 0.35$. When residual oil is hydrodesulfurized, the catalysts in which more favorable conditions exist for the performance of slow sites will be more efficient. The number of these sites should be as great as possible. The increased concentration of Co or Ni in the active phase ($r > 0.35$) should satisfy the above conditions. Hence, it is clear that it is impossible to create a catalyst possessing the highest densities of the vacancies of both types.

2. Effect of Temperature on the Performance of Active Sites

Unpromoted Mo/Al_2O_3 catalysts. Figure 6 shows data on the radioisotope testing of the unpromoted molybdenum catalysts in the range 300–400°C. As can

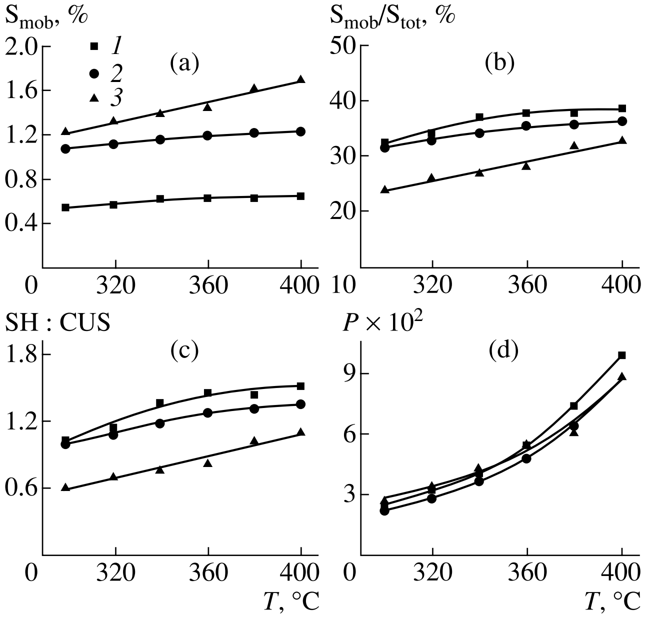

Fig. 6. Temperature dependences of (a) the amount of mobile sulfur S_{mob}, (b) the ratio between the amount of mobile sulfur and that of total sulfur S_{mob}/S_{tot}, (c) the SH : CUS ratio, and (d) the productivity of active sites obtained during radioisotopic testing of $Mo^{35}S_2/Al_2O_3$ catalysts containing (*1*) 4, (*2*) 8, and (*3*) 12% Mo.

be seen in Fig. 6a, the amount of mobile sulfur in samples containing 4 and 8% Mo grows slowly and levels out onto a plateau at temperatures above 360°C. A linear plot of the concentration of mobile sulfur vs. temperature is typical of the 12% Mo catalyst. The same plots are observed for the temperature change in the fraction of mobile sulfur in the total amount of sulfide sulfur (Fig. 6b) and the SH : CUS ratio (Fig. 6c).

Note that the variations in the S_{mob}/S_{tot} and SH : CUS values with increasing temperature are described by the same functions. Since S_{mob} = SH, mobile sulfur is the surface SH groups participating in hydrogen sulfide formation and the total amount of sulfide sulfur S_{tot} is a constant value detectable in the sample before hydrodesulfurization. Therefore, the CUS number in the unpromoted Mo catalysts is virtually independent of the reaction temperature. Only the number of SH groups capable of participating in H_2S formation increases with temperature. Therefore, the SH : CUS ratio increases. However, although the total number of CUSs (V + ES) is independent of temperature, the ratio between the functioning vacancies and empty sites remarkably changes: the number of functioning vacancies increases and the number of empty sites decreases with an increase in temperature.

An increase in the amount of mobile sulfur with an increase in temperature indicates that, along with SH groups, which can be detected experimentally, some amount of SH groups, which are inactive at this temperature but become active with increasing reaction temperature, are present on the catalyst surface. Within the framework of our studies, this amount can be evaluated within the limits of 10–25%. These “inactive” SH groups implicitly enter the CUS number or, more precisely, the ES number, and, hence, the real number of ES should be somewhat less than the calculated one. The reasons for the above decrease in the ES number with increasing temperature can be twofold: (1) the activation of empty surface and formation of new functioning vacancies and (2) the involvement of SH groups that are inactive at lower temperatures in the reaction. It should be noted that this correction does not affect the productivity of an active site and the number of vacancies.

As can be seen in Fig. 6d, the productivities of active sites in the catalysts with various Mo concentrations are close and characterized by similar temperature dependences. That is, the catalysts with various Mo concentrations contain the same active sites and only differ in the proportions between the numbers of SH groups, empty sites, and functioning vacancies. A slow increase in the amount of mobile sulfur with increasing temperature and the exponential growth of the productivity of active sites give evidence that the catalytic activity of Mo catalysts is due to the activation of the Mo–SH bond in the whole temperature range under study.

Promoted $CoMo/Al_2O_3$ catalysts. Findings of the radioisotopic testing of promoted $CoMo/Al_2O_3$ catalysts at different temperatures are shown in Fig. 7. As follows from these data, a linear correlation exists between the thiophene conversion and the amount of mobile sulfur in the catalyst (Fig. 7a). That is, the catalytic activity is determined, to a first approximation, by the amount of mobile sulfur in the catalyst. Previously, we often observed similar dependences. However, this relationship is only valid in cases when the nature of the active sites of the catalyst under comparison is the same and the productivities of the corresponding sites differ only slightly.

The effect of the reaction temperature on the SH groups : CUS ratio in the Mo and CoMo catalysts is different (Fig. 7b). In the first case, the SH : CUS ratio monotonically increases with temperature. In the case of the CoMo catalysts, a plateau is observed at 320–350°C. The above ratio sharply increases with a further increase in the reaction temperature. This pattern is due to a change in the amount of rapid sulfur (rapid SH groups). This conclusion can be drawn based on comparison of Figs. 7b and 7c. While the amount of slow sulfur is practically independent of temperature, the temperature dependence of the concentration of rapid sulfur repeats exactly the shape of the curves in Fig. 7b. Thus, the coverage of the active phase surface in the CoMo catalyst with SH groups is determined by the amount of rapid SH groups.

The S-like shape of the curves for rapid sulfur and the linear temperature dependence of the amount of functioning vacancies V_{rapid} (Fig. 7d) show that some amount of V_{rapid} appears in the temperature range 320–350°C when the amount of surface SH groups is the same. The productivity of rapid sites increases in this temperature range (Fig. 7e). Thus, the catalytic activity in the temperature range 320–350°C is determined by the activation of the M–SH bond similarly to that in the unpromoted Mo catalysts. At higher temperatures, an increase in the productivity of rapid sites slows down and the curves level out onto a plateau. Simultaneously, the relative number of functioning rapid sites continues to increase. In other words, the activation of the M–SH bond does not determine the increase in the catalytic activity at temperatures above 350°C. A factor that limits hydrogen sulfide formation should exist. The molecular hydrogen adsorbed on the catalyst probably plays this role. According to the mechanism of thiophene hydrodesulfurization proposed in [40, 43, 46], the rupture of the H–H bond during interaction of molecular hydrogen with SH groups is the rate-determining step (Fig. 1).

At low temperatures, excess molecular hydrogen is adsorbed on the catalyst surface, and H_2S formation and thiophene hydrogenolysis are limited by the mobility of SH groups (activation of the M–SH bond) and the number of functioning vacancies. The amount of adsorbed molecular hydrogen decreases with temperature and its deficiency arises, which limits hydrogen sulfide formation. The question arises as to why the deficiency in the adsorbed molecular hydrogen only limits the performance of rapid sites in the promoted CoMo catalysts and does not affect the performance of active sites of the unpromoted Mo catalyst at the same temperatures. The answer can be found based on comparison of productivities of these sites at the same reaction temperatures or, phrased differently, on the number of H_2S molecules formed with the participation of one SH group by passing a thiophene pulse of 1 μl over 100 mg of the catalyst. Note that the productivities of rapid sites of the CoMo catalysts are nearly 3–4 times higher than the productivities of active sites of the Mo catalysts. Hence, the rapid sites of the CoMo catalyst need more molecular hydrogen than the sites of the Mo catalyst. The low-productivity active sites do not "feel" the deficit of adsorbed molecular hydrogen at temperatures below 380°C.

3. Radioisotopic Testing in Catalyst Screening for Processing Light and Heavy Oil Fractions

We attempted to apply the developed concept of the interrelation between the catalyst composition, the density of functioning vacancies, the productivity of the active sites of various types, and the nature of crude to develop criteria for preliminary catalyst selection.

Based on the data of radioisotopic testing of the model and commercial catalysts, we constructed contour diagrams (Fig. 8) for the density of the functioning vacancies for rapid and slow sites.

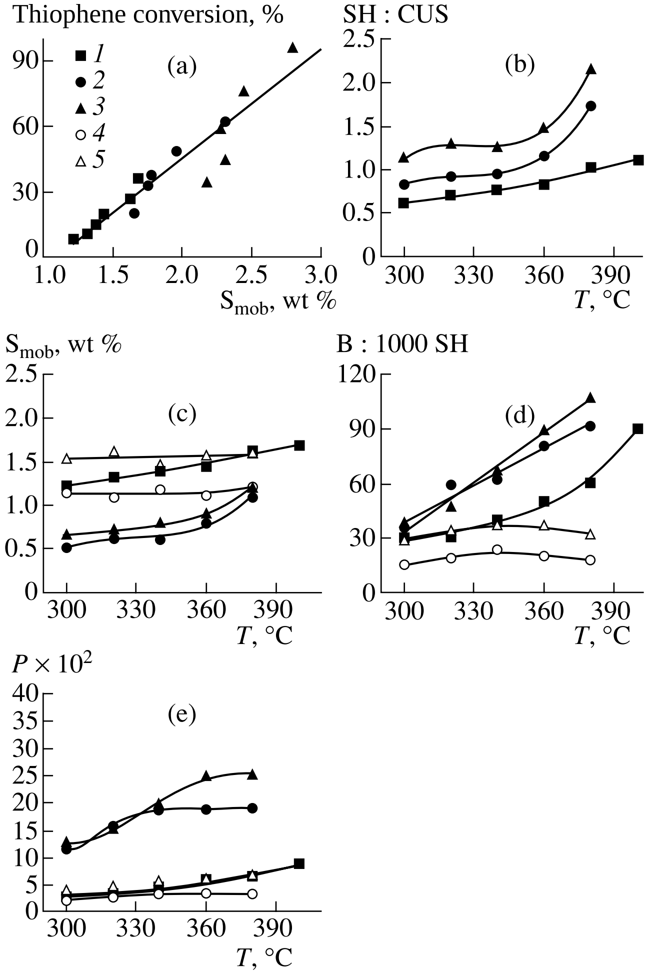

Fig. 7. (a) A plot of the thiophene conversion vs. the amount of mobile sulfur S_{mob} and the temperature dependences for (b) the SH : CUS ratio, (c) the amount of mobile sulfur S_{mob}, (d) the number of functioning vacancies V based on 1000 SH groups, and (e) the productivity of the active sites obtained from radioisotopic testing of $CoMo^{35}S/Al_2O_3$ of various compositions: (*1*) 12% Mo; (*2*, *4*) 12% Mo, 2% Co; and (*3*, *5*) 12% Mo, 4% Co. Curves *2*, *3* are for rapid sites and *4*, *5* are for slow sites.

As can be seen in the diagram (Fig. 8a), almost all commercial catalysts are characterized by a high density of rapid vacancies. However, catalysts 3, 5, and 7 possess the V_{rapid} vacancies with the highest density. Catalyst 1 possesses the highest density of V_{slow} vacancies, and catalysts 9 and 10 are characterized by somewhat lower values (Fig. 8b). The other catalysts are inferior in V_{slow} vacancies to the latter three catalysts. One may suggest that catalysts 3, 5, and 7 will be most active in processing light oil fractions and catalysts 1, 9, and 10 will be most active in processing heavy oil.

The catalysts cited were tested in a pilot regime in the hydrodesulfurization of gasoline and diesel fractions (Fig. 9). As follows from the figure, catalysts 3, 5, and 7 are most active in the hydrodesulfurization of

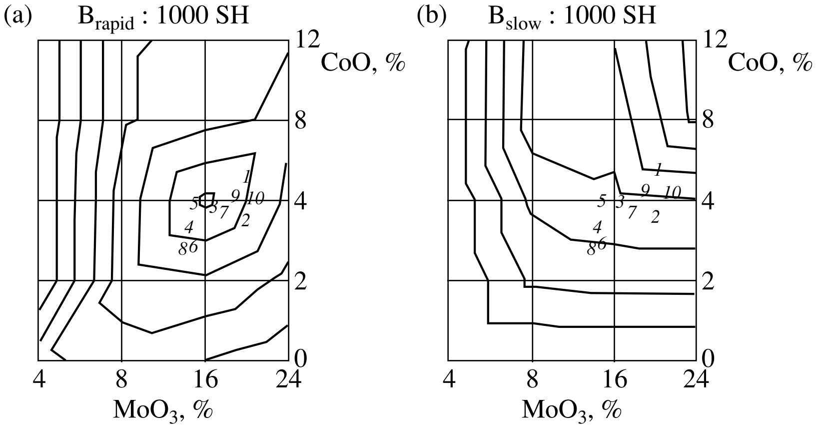

Fig. 8. Contour diagrams of the distribution of (a) rapid and (b) slow vacancies in the commercial catalysts according to the data of radioisotopic testing. The numbers of the commercial catalysts tested are shown. The number of a catalyst corresponds to that in Fig. 9.

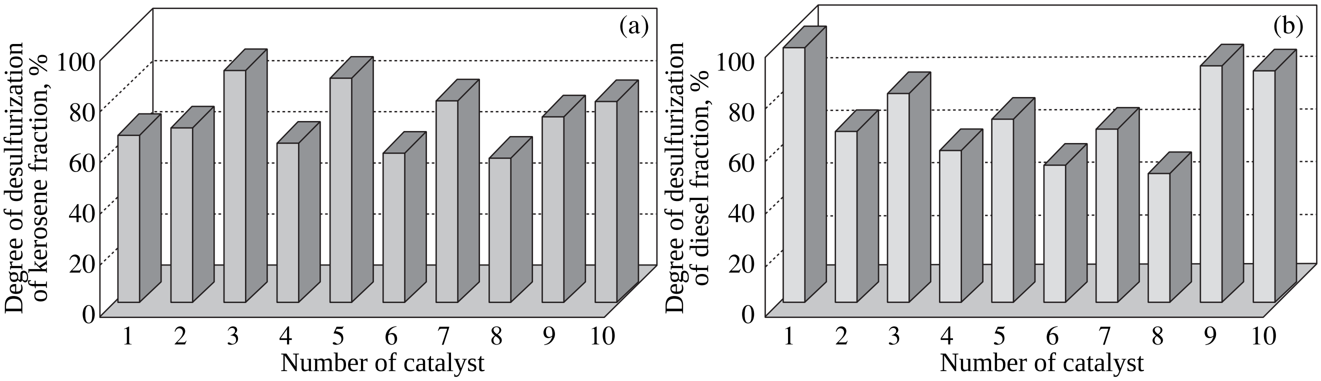

Fig. 9. Results of pilot testings of the commercial catalysts in hydrodesulfurization of (a) kerosene fraction and (b) diesel fuel. The number of a catalyst corresponds to that in Fig. 8.

gasoline, whereas catalysts 1, 9, and 10 are most active in the hydrodesulfurization of diesel fuel.

Comparison of data from radioisotopic testing with those of pilot testing gives strong evidence that correlations exist between the catalytic activity in hydrodesulfurization of various crudes and the density of vacancies of the corresponding type. In other words, the radioisotopic monitoring allows one to choose catalysts for the following pilot testing.

4. Use of the Method of Radioisotopic Testing of CoNi Catalysts for Residual Oil Hydrotreating

Selections of the objects for research. As shown in Section 1, an increase in the promoter concentration in the CoMo catalysts leads to a decrease in the amount of rapid sulfur but enhances the concentration of slow sulfur. We attribute the first sulfur to the sites belonged to Mo and the second sulfur to the Co sites. In Section 1, we suggested on the basis of the systematic monitoring of the active sites of the CoMo catalysts that heavy oil processing requires a maximal amount of slow sites on the catalyst surface. In the threshold case, the catalyst should not contain Mo at all. However, the Co catalysts are in fact much less active in hydrodesulfurization than the Mo-containing catalysts. At the same time, the hydrogenating properties of Co and Ni sulfides are well known. The resistance of cobalt catalysts to catalytic poisons is an argument in favor of choosing them.

Results of radioisotopic testing. Preliminary runs showed that the amount of sulfide sulfur in all the samples with a nickel concentration from 2.5 to 11%, which were sulfided with H_2S/H_2, almost reached the stoichiometric values. The concentration of sulfide sulfur in the Co catalysts was higher than its stoichiometric concentration in the Co_9S_8 phase. In the samples with a low cobalt concentration, the concentration of sulfide sulfur was higher than the stoichiometric value by 100%. For example, the concentration of sulfide sulfur in the 3.4% Co/SiO_2 sample was 3.7%, whereas the stoichiometric amount of sulfur in the Co_9S_8 phase at this Co concentration is 1.64%. We supposed that the CoS_2 phase, which was observed in the $CoMo/Al_2O_3$ catalysts by some authors [60, 61], exists in the catalyst. In the cat-

Table 3. Results of radioisotopic testing and data on heavy residue hydrotreating over the Co(Ni) and Mo-containing catalysts (Reaction temperature 360°C)

No.	Catalyst composition	Results of radioisotopic testing*										Results of the runs on residual oil hydrotreating				
		Sulfiding agent	S_{stoich}	S_{tot}	S_{mob}	S_{mob}/S_{tot}, %	γ, %	$P \times 10^2$	CUS : SH	V**	ES**	Treatment	Degree of desulfurization, wt %	Degree of demetallation, wt %	Residual asphaltens, wt %	Coke deposition, wt %
1a	(7.0% Co)/Al_2O_3	TP	3.80	1.16	1.16	100	5.4	1.89	1 : 0.44	19	2250	r	26.0	80.0	2.1	2.8
1b	(7.0% Co)/Al_2O_3	H_2S	3.80	5.5	0.89	16.2	5.3	2.43	1 : 0.31	24	3228	s	19.4	80.0	2.0	3.5
2a	(7.4% Co)/SiO_2	TP	4.01	2.42	2.42	100	8.0	1.34	1 : 1.52	13	644	r	55.7	95.6	0.5	2.0
2b	(7.4% Co)/SiO_2	H_2S	4.01	5.7	0.63	11.1	4.0	2.56	1 : 0.19	26	5324	s	13.6	89.0	1.3	3.5
3a	(7.6% Ni)/Al_2O_3	TP	4.12	1.03	1.03	100	8.4	3.33	1 : 0.33	33	2977	r	18.0	82.0	1.2	5.0
3b	(7.6% Ni)/Al_2O_3	H_2S	4.12	4.0	1.38	34.5	15.7	4.63	1 : 0.50	46	1954	s	30.8	80.0	2.0	6.8
4a	(7.3% Ni)/SiO_2	TP	3.96	0.82	0.82	100	4.3	2.10	1 : 0.26	21	3801	r	16.5	90.5	1.0	3.0
4b	(7.3% Ni)/SiO_2	H_2S	3.96	3.76	1.23	32.7	7.3	2.34	1 : 0.45	24	2191	s	28.0	78.0	1.8	3.4
5a	(3.4% Co + 4.1% Ni)/Al_2O_3	TP	4.07	1.34	1.34	100	7.6	2.30	1 : 0.49	23	2024	r	21.5	76.0	2.7	3.2
5b	(3.4% Co + 4.1% Ni)/Al_2O_3	H_2S	4.07	4.82	2.16	45.0	17.0	3.19	1 : 1.14	32	847	s	46.0	61.0	3.8	4.6
6a	(3.5% Co + 3.5% Ni)/SiO_2	TP	3.80	1.25	1.25	100	5.4	1.73	1 : 0.49	17	2012	r	27.0	79.0	2.4	2.4
6b	(3.5% Co + 3.5% Ni)/SiO_2	H_2S	3.80	4.1	0.95	23.2	4.2	2.03	1 : 0.33	18	2969	s	20.5	76.0	2.6	2.8
7	(8.0% Mo)/Al_2O_3	S	5.33	3.38	1.20	34.9	14.3	4.9	1 : 1.24	49	758	s	17.2	64.1	1.1	5.9
8	Ni-Mo/Al_2O_3	H_2S	9.38	6.08	2.49	41.0	59.0	P_{rapid} = 20.1	1 : 4.99	V_{rapid} = 43	84	s	32.9	75.5	2.8	10.5
	Commercial catalyst							P_{slow} = 5.4		V_{slow} = 74						

Note: TP, thiophene; r, reduction; s, sulfiding after reduction.

* Approximate contact time is 3 s.

** Per 1000 SH groups.

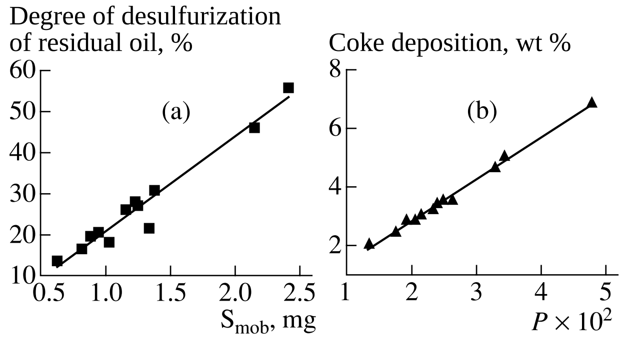

Fig. 10. (a) Degree of residual oil desulfurization vs. amount of mobile sulfur in the catalyst and (b) coke deposition vs. productivity of active sites.

alysts 5.7% Co/SiO_2 and 11% Co/SiO_2, the concentration of sulfide sulfur was 1.5 times higher than that of the stoichiometric sulfur in the Co_9S_8 phase: 5.7 and 8.63% (3.57 and 5.3%, respectively). It is possible that in the Co catalysts sulfided with H_2S, the phase of a mixed composition, 50% Co_9S_8 and 50% CoS_2, is formed. The plots of the catalytic activity of the samples studied vs. the concentration of the active component pass through a maximum at 7.0–7.6% Co. Therefore, the samples of the catalysts with these metal concentrations were studied in more detail.

All the curves for a change in the molar radioactivity of hydrogen sulfide obtained by radioisotopic testing were described by monoexponential equations. Hence, the catalysts containing Co or Ni or Co + Ni possess the same sites for H_2S formation. It follows from Table 3 that the treatment of the reduced catalyst with an H_2S/H_2 mixture always leads to more complete sulfiding than when thiophene is used as a sulfiding agent.

For completely sulfided catalysts it was found that only a part of sulfide sulfur participated in thiophene hydrogenolysis and was mobile. Its fraction varied from 11 to 50% and was higher in the samples containing Ni or Ni + Co than in the Co catalysts. This is valid for the catalysts supported on both Al_2O_3 and SiO_2 and is likely due to the higher dispersion of the Ni sulfide particles compared to the Co sulfide particles and to the possible formation of the CoS_2 phase. The fraction of mobile sulfur in the Co/Al_2O_3 catalysts sulfided with H_2S/H_2 is higher than in similar samples containing SiO_2. This may possibly be explained by the higher dispersion of the sulfide particles supported on Al_2O_3 compared to the SiO_2-supported sulfide particles.

Unlike sulfiding with H_2S/H_2, treatment with thiophene did not result in maximally possible stoichiometric values. The total sulfide sulfur formed upon sulfiding with thiophene was mobile, that is, participated in H_2S formation.

It follows from comparison of the Co/SiO_2 and Co/Al_2O_3 catalysts sulfided in the same way that the productivities of active sites in the samples are close. This may indicate an insignificant effect of the nature of the support on the reactivity of active sites of these catalysts and the substantial influence of the support on the amount of these sites.

The effect of the nature of the metal on the productivity of active sites of the catalysts is well seen in the series Co–(Co + Ni)–Ni. Note that the productivity of active sites in all the catalysts supported on the same carrier and sulfided in the same way increases in the series Co < (Co + Ni) < Ni. Hence, SH groups on Ni sulfide particles are more reactive in H_2S formation during thiophene hydrogenolysis than the same SH groups bound to Co.

We evaluated the ratio between the concentrations of the surface SH groups and CUS and the relative ratios between the numbers of functioning vacancies, empty sites, and SH groups. We assumed that the particles of CoNi sulfide in the CoNi catalysts form a more disperse phase than the MoS_2 or CoMoS clusters [62–65] because the CoMoS phase, in which sulfur and metal are distributed layer-by-layer and a significant part of the sulfur occurring in the depth of the "sandwich" is inactive, is not formed. One may suggest that in the CoNi catalysts nearly all the sulfide sulfur that enters the Co and Ni sulfides is potentially capable of participating in the reaction, that is, is mobile. Calculations showed (Table 3) that the density of the functioning vacancies in most CoNi catalysts is somewhat lower than in the unpromoted Mo sample with a close concentration of active metal (sample 7) and in the commercial $NiMo/Al_2O_3$ catalyst (sample 8). The exceptions are samples 3a, 3b, and 5b. Note that the coverage of the active phase surface in the CoNo catalysts with SH groups is low: the CUS : SH ratio in most samples is substantially higher than unity and the ES number is significantly higher than that in the Mo-containing catalysts (cf. data in Table 1). The exceptions are samples 2a and 5b in which the CUS : SH ratios and the ES fraction are close to the corresponding values for the 8% Mo/Al_2O_3 catalyst.

The results of the radioisotopic testing make it possible to distinguish four catalysts: 2a, 3a, 3b, and 5b. Sample 2a contains the largest amount of mobile sulfur and SH groups, although the productivity of active sites of this catalyst is the least among the catalysts under study and the thiophene conversion is low. Sample 5b exhibited the highest thiophene conversion, whereas the amount of mobile sulfur in it is practically the same as in sample 2a and the productivity of active sites is substantially higher than that of most catalysts under consideration. Sample 5b is also characterized by a high coverage of the surface with the SH groups and by a high density of functioning vacancies. Sample 3a possesses a high density of functioning vacancies, but the coverage of the surface with the SH groups is negligible. Finally, sample 3b has the maximal productivity of active sites and high thiophene conversion with a relatively small amount of mobile sulfur. In addition, the density of functioning vacancies in it is maximal, whereas the coverage of the surface with SH groups is low. We attempted to estimate the effect of the above parameters on the catalyst performance under real conditions by comparing with data obtained in the hydroconversion of real crude.

Comparative analysis of radioisotopic testing data and data on residual oil hydrotreating. It follows from comparing radioisotopic testing data with the data on residual oil hydrotreating that the degree of residual oil desulfurization linearly depends on the amount of mobile sulfur on the catalyst (Fig. 10a). We noted in Section 2 that the linear plot of the thiophene conversion vs. the mobile sulfur amount in the CoMo catalysts was obtained for the catalysts in which the active sites are characterized by close productivities. A variety of organosulfur compounds in the real crude, which underwent desulfurization, including large molecules, and the presence of compounds with different resistances to destruction seem to align the productivities of active sites of various catalysts. On this basis, one might conclude that the productivity of the active sites is unimportant for processing real crude. However, this is not the case. We unexpectedly found another linear dependence, namely, the dependence between the productivity of active sites and coke formation, the latter being the secondary process with respect to hydrodesulfurization and H_2S formation (Fig. 10b). Such a dependence may be due to the effect of the support acidity on coking and hydrodesulfurization. The relation between the support acidity and coking is well known, and many authors observed the dependence of the catalytic activity on the support acidity (see, for instance, [66, 67]). It follows from Table 3 that the samples with close compositions and prepared by the same sulfiding procedure but supported on different carriers differ in the degree of coking and the productivity of active sites. These parameters are higher for the catalysts supported on Al_2O_3 than for those supported on SiO_2. However, this fact explains the above dependence only in part. For instance, the higher tendency of the Ni-containing catalysts to coking cannot be explained by their acidity. Possibly, the higher the productivity of an active site, the greater the number of hydrocarbon fragments formed upon destruction of organosulfur molecules and the more intense the coking.

This suggestion is confirmed by the comparison of the results of residual oil hydrotreating over the Mo-free catalysts and $NiMo/Al_2O_3$ commercial catalyst (sample 8, Table 3). Sample 8 displays a high desulfurizing ability, which is only inferior to samples 2a and 5b, but is poorly active in demetallation and readily coked. Sample 8 contains active sites of two types, rapid and slow, whose productivities are 20.1×10^{-2} and 5.4×10^{-2}, respectively, and the number of rapid sites is 25% of the sum of rapid and slow sites. The amount of mobile sulfur is 41% of the whole sulfide sulfur in the sample. Thiophene conversion over this sample was 59% under the same experimental conditions as on the rest of the catalysts, and this value is substantially higher than that on other samples containing no Mo. The total concentration of active sites in the promoted catalyst increases compared to the unpromoted catalyst due to an increase in the number of slow sites. Rapid sites increase the catalytic activity and simultaneously facilitate catalyst coking. This is of special importance for processing heavy oil. It is this fact that we observed during residual oil hydrotreating over sample 8: the total amount of mobile sulfur in the sample is high (as in sample 5b), and this results in the high desulfurizing activity, whereas the high productivity of part of the active sites leads to enhanced coking. The systems in the upper right part of Fig. 10a and the bottom left part of Fig. 10b should show the best performance in heavy residue hydrotreating. This is the case for samples 2a and 5b. These catalysts are characterized by the highest coverages of the active phase with SH groups. At the same time, the density of vacancies in catalyst 5b is lower than that in 3a and 3b, and this value in sample 2a is the lowest. This means that the active component in the systems containing no Mo in which the CoMo phase is not formed is distributed on the catalyst surface more uniformly compared to the analogous Mo-containing systems. A significant fraction of the active phase surface of the CoNi samples is not occupied by SH groups. As a result, the optimal CUS : SH ratio, which is equal to ~1–2 and even 3 for some commercial samples, is not reached. This is the probable reason why most of the NiCo catalysts are less active than the Mo-containing catalysts. Therefore, the coverage of the active surface with mobile SH groups is the determining factor for the catalytic activity of these systems. Samples 2a and 5b satisfy this criterion.

Comparison of the Mo-containing sulfide catalysts with the Mo-free catalysts shows that when the CoMoS phase is formed, a comparatively high coverage of the surface with the SH groups is reached and the density of the functioning vacancies V_{rapid} and V_{slow} is the determining factor for the catalytic activity. When the catalysts contain no Mo(W) and the CoMoS phase is not formed, the coverage with SH groups is insufficient. In this case, the catalytic activity will be determined by the number of these SH groups rather than by the number of the functioning vacancies.

Hence, to choose catalysts for light oil hydrotreating, it is necessary to produce highly active sites on the catalyst surface. Contrary to this, to choose the most efficient catalysts for heavy oil hydrotreating, one should prefer the systems with a great amount of mobile sulfur, that is, with a relatively high number of low-productivity active sites.

CONCLUSIONS

The systematic radioisotopic testing of sulfide CoMo catalysts in thiophene hydrodesulfurization allows us to draw the following conclusions.

(1) The activity of the CoMo catalyst is determined by both the productivity of active sites and by the number of vacancies for thiophene adsorption.

(2) The temperature effect on the performance of the active sites of the unpromoted Mo catalysts manifests itself in the Mo–SH bond activation in the whole temperature range from 300 to 400°C. The catalytic activity of the CoMo catalysts below 350–360°C is determined by the activation of the Mo–SH bond and at higher temperatures by the amount of molecular hydrogen adsorbed on the active phase surface.

(3) An increase in the Co concentration in the CoMo catalysts results in a decrease in the number of surface SH groups linked to Mo because of the partial blocking of Co with sulfide species and an increase in the number of the SH groups bound to Co. Simultaneously, the productivity of Mo-bound sites increases up to the degree of promotion r = Co/(Co + Mo) = 0.33 and then remains constant.

(4) An increase in the Mo concentration in the catalyst leads to an increase in the CUS : SH ratio. The introduction of Co slightly affects this ratio.

(5) The highest density of functioning vacancies V_{rapid} belonged to Mo corresponds to the degree of promotion $r = 0.25–0.33$. A further increase in the Co concentration results in its decrease. The density of the functioning vacancies V_{slow} bound to Co reaches the highest values at $r > 0.33$.

(6) relatively high coverage of the active phase surface with the SH groups is reached in the CoMoS catalysts, and the density of the functioning vacancies V_{rapid} and V_{slow} is the determining factor for the catalytic activity. When the catalysts contain no Mo, the catalytic activity is determined by the number of SH groups rather than by the number of the functioning vacancies.

The criteria for the evaluation of the efficiency of the catalyst performance under conditions of hydrodesulfurization of different crudes were elaborated. The data on the pilot testing of commercial catalysts provide evidence for the adequacy of the criteria developed.

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