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Concept of acid–base catalysis by metal sulfides

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ABSTRACT

The structure of the active component of the sulfide hydrodesulfurization (HDS) catalysts is considered. The active component consists of a single slab of MoS_2 (WS_2) with Ni or Co atoms being located in its edge plane. The essential element of the active component is hydrogen occluded into the MoS_2 matrix, which localizes in the center of “empty” trigonal prism of a MoS_2 matrix made from six sulfur atoms under Ni (Co) atom at the distance of 1.5 Å. Occluded hydrogen appeared in the active component during the catalyst sulfidation as a result of its oxidative addition to the Ni (Co) atoms. This occluded hydrogen creates an electronic d^6 configuration of Ni(IV) or Co(III) atoms, which are the Lewis acid sites with two vacant d_{z^2} and d_{xy} orbitals. Therefore, these active centers can adsorb donor molecules of thiophene. The activation of hydrogen occurs on the couplet sulfur atoms at the edge planes of a single MoS_2 (WS_2) slab. The driving force of this process is the presence of the S–S chemical bond at the terminal sulfur atoms that restrict an electrically neutral macromolecule of the active component and act as the Lewis basic sites. An excess of electron density is transferred from these atoms to a hydrogen molecule, which results in its homolytic dissociation. The high rate of catalytic transformation is ensured by the fast transfer of electrons and protons along the system of chemical bonds within an electrically neutral macromolecule of the active component.

1. Introduction

There are two acid–base theories in chemistry for homogeneous phases: the Brønsted theory and the Lewis theory. Both are applicable for surface science and heterogeneous catalysis. Following the first theory, acid is a substance that can donate proton, while base is a substance that can accept proton and, therefore, must contain a lone pair of electrons. According to the Lewis theory, an acid is any species with a vacant orbital that can accept a pair of electrons from another atom to form a new bond. On the other side, a base is a substance that can donate a pair of electrons to another atom to form a new bond [1]. This paper demonstrates that the mechanism of C–S bond hydrogenolysis reaction with sulfide hydrotreating catalysts can be described in the frame of Lewis acid–base catalysis.

Hydrotreating of oil fractions is the largest-scale process in the petroleum refining industry. Hydroprocessing includes a variety of catalytic reactions in hydrogen atmosphere to remove heteroatoms from crude oils and to hydrogenate unsaturated compounds and, partially, aromatics in petroleum feedstocks. The most important process is the C–S bond hydrogenolysis reaction to remove sulfur, therefore hydrotreating catalysts are frequently referred to as hydrodesulfurization (HDS) catalysts. All these processes proceed on the bimetallic sulfide Ni(Co)–Mo(W) catalysts both bulk and supported on different carriers, which can contain different modified elements. All aspects of technologies, catalyst characterization and active components models are summarized in [2,3]. Reaction mechanisms are reviewed in [3,4]. Let us consider the geometric and electronic structure of the active component of HDS catalysts.

2. The geometric structure of the active component of the sulfide HDS catalysts

Among all models of the active component structure reviewed in [2,3], one can single out the models that are based on the conception of a MoS_2 single slab with Ni (Co) atoms being localized in its edge plane. However, the position of Ni (Co) atoms and their role in catalysis is a subject of discussion for many years. Here we omit details of this discussion (they are considered in [3,4]) and focus our attention on the model of “sulfide bimetallic species” (SBMS) developed at the Boreskov Institute of Catalysis (Fig. 1) [3,4]. The SBMS model differs from other similar models in a number of points which are listed below:

1. The necessary and sufficient structural element of SBMS consists of a single slab of MoS_2 (or some other disulfide that crystallized in the molybdenite structural type) with ions of a transition

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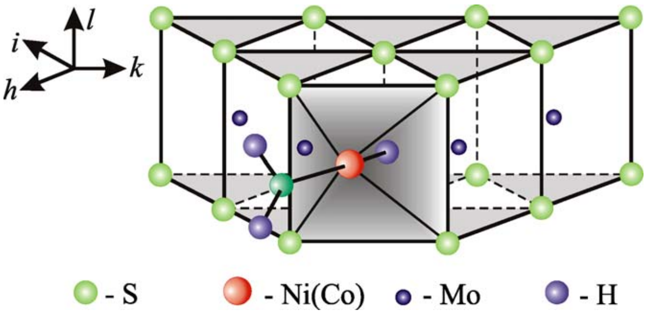

Fig. 1. Structure of the active component of the sulfide HDS catalysts with the occluded hydrogen atom and the adsorbed H_2S molecule.

metal (Ni, Co or any other metal that can interact with the sulfide matrix) which effectively interact with four sulfur ions in the $(1\,0\,\bar{1}\,0)$ plane of a MoS_2 matrix. In such a case, the Ni (Co) atoms are located in the center of a square pyramid of sulfur atoms; the distance from the base plane to the Ni (Co) atoms is 0.5 Å (Fig. 1).

2. The second essential element of SBMS is hydrogen occluded into the MoS_2 matrix. Occluded hydrogen appeared in the active component during the catalyst sulfidation because of its oxidative addition to the Ni (Co) atoms [5–8]. It localizes in the center of "empty" trigonal prism of a MoS_2 matrix made from six sulfur atoms under Ni (Co) atom at the distance of 1.5 Å (Fig. 1).
3. The Ni (Co) ions are the catalyst active sites (not "promoters"!). Their electronic structure is considered in the next section of the paper.
4. The bimetallic sulfide species is an electrically neutral macromolecule and is realized in both bulk and supported catalysts.

3. The valence state of metals in the active component of HDS catalysts

The electronic structure of the transition metal atom (or ion) is a key factor that defines the catalytic activity of any catalysts, because it determines the ability for coordination of a substrate molecule. However, the valence state of metal atoms in the active component of HDS catalysts has not been considered in the literature. A direct experimental investigation of the formal oxidation state of metal atoms is allowed by the X-ray photoelectron spectroscopy (XPS). Nevertheless, when being applied to the highly dispersed supported catalytic systems including sulfide catalysts, this technique meets some restrictions because of non-uniform composition of surface species (see e.g. [2] and refs. therein).

We have found many years ago that, in the sulfide bimetallic catalysts prepared via metal complex precursors, the position of the Ni (Co) lines in the X-ray photoelectron spectra is shifted to the higher values of binding energies (BEs) in comparison with those of binary sulfides of the same metals [9]. It was especially strange, because we had to expect that at high temperature and high hydrogen pressure, the Ni or Co atoms must be reduced to form a lower oxidation state. Nevertheless, we observed an opposite effect, which regularly reproduces itself in different catalytic systems: silica [9], alumina [10,11] and carbon [6] supported bimetallic sulfide catalysts, bulk sulfides Ni/WS_2 [12,13], Co/MoS_2, Co/WS_2, Ni/ReS_2, and Cu/WS_2 [13].

We undertook a special study to answer the question on valence state of the active metal atoms (Figs. 2 and 3) [6]. In the alumina supported sulfide catalysts, the Mo3d line is characterized by a narrow poorly resolved doublet with the $Mo3d_{5/2}$ BE exactly as in both bulk and highly dispersed MoS_2 (Fig. 2). The position of this line does not change after heating in the spectrometer chamber in vacuum or in the atmosphere of $(H_2 + H_2S)$. For the Sibunit supported catalysts (Fig. 3), this line is a well-resolved doublet, but its position is shifted towards higher BEs. This shift seems to result from the chemical interaction of the active component with the support surface [14]. Of importance is that the line position does not change after the *in situ* heating neither in vacuum, nor in hydrogen, nor in the $(H_2 + H_2S)$ atmosphere.

At the same time, the Ni2p line changes its position essentially after the *in situ* thermal treatments (Figs. 2 and 3). The Ni2p line of the freshly *ex situ* sulfided bimetallic catalysts is shifted by 1.0 eV to higher BEs with respect to the highly dispersed NiS/Al_2O_3. In the Sibunit supported bimetallic sulfide catalysts this line is shifted in the same direction even more. After sulfide catalysts vacuuming at 300–500 °C to residual 10^{-10} Torr, the Ni2p line is shifted by 1.0–1.2 eV to the lower BEs for both catalysts. The magnitude of the shift exceeds considerably the BE measurement accuracy and corresponds to the Ni2p line position in the highly dispersed NiS. Note that this line position does not change after sample treatment with hydrogen at 300–400 °C. The treatment of the vacuumed sample with the $(H_2 + H_2S)$ mixture at 300–450 °C in the spectrometer chamber shifts the Ni2p line by 0.5–0.7 eV back to the higher values of BEs. This change in the Ni2p line position seems to be reversible and is observed after repeated treatments. The similar treatment of the highly dispersed NiS/Al_2O_3 catalyst results in another regularities (for details see [6]). The similar observation in the positive shift of the Ni2p BEs was made for the bulk Ni/WS_2 catalysts [15].

To explain an unusually high formal positive charge of the Ni (Co) atoms, we suggested an oxidative addition of dihydrogen to the Ni or Co ions to occur during sulfiding the catalyst (see next paragraph). Actually, the evacuation at high temperature of the sulfide catalysts results in a *reductive elimination of hydrogen*, therefore we observe a shift of the Ni2p line to the lower values of binding energy. A consecutive treatment of the same evacuated sample with the $(H_2 + H_2S)$ mixture at 300 °C causes the *oxidative addition of hydrogen*, therefore we observe a shift of this line to the higher values of binding energy. An exposure of the freshly sulfided catalysts to air results in the oxidation of occluded hydrogen, therefore we observe the reduction Ni(IV)→Ni(II).

Another significant conclusion was drawn from the quantum-chemical investigations: the electron density from the Ni(IV) or Co(III) atoms is transferred to the neighboring S atoms, but not to the adjacent Mo atoms, as might be expected. Therefore, we did not observe any changes in the Mo3d line position during thermal treatments of sulfide catalyst inside a XPS spectrometer chamber as was discussed above.

4. Oxidative addition of hydrogen in the sulfide catalysts

The oxidative addition of hydrogen to square-planar Ir(I) complexes was discovered over 40 years ago [16] and is now one of the key reactions in homogeneous catalysis [17]. In particular, it is well known that this reaction is the first step in the formation of active sites in the alkene hydrogenation catalysts [18]. In such a case, hydrogen acts as a unique molecule that simultaneously displays both reductive and oxidative properties under the same catalytic reaction conditions.

Unfortunately, there are so far no direct experimental methods for studying the nature of transient species formed upon adsorption of substrate on the active sites of real heterogeneous catalysts. Therefore, we will refer to analogies in the structures and mechanisms of action of homogeneous catalysts and our approach is based on the concept of the common nature of homogeneous, heterogeneous and enzyme catalysis [19–21].

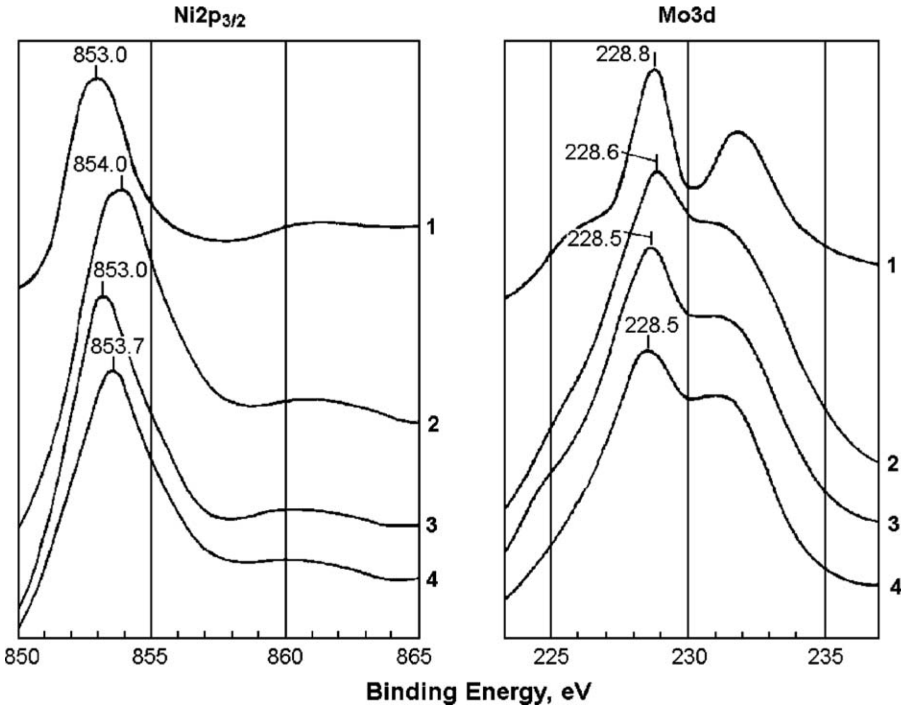

Fig. 2. XPS data on the electronic state of the Ni and Mo atoms in the active component composition of the sulfide (Ni,Mo)/Al_2O_3 catalysts. (1) NiS/Al_2O_3 catalyst and mechanical mixture (MoS_2 + Al_2O_3); (2) the (Ni,Mo)/Al_2O_3 catalyst is sulfided *ex situ* at 400 °C; (3) the previous sample is evacuated *in situ* at 300 °C until residual pressure of 5×10^{-9} Torr; and (4) the previous sample is sulfided *in situ* in the (H_2 + H_2S) mixture at 300 °C. (Taken from [6].)

The possibility of oxidative addition of hydrogen to an active metal atom within the active component of sulfide catalysts was shown by non-empirical quantum-chemical methods, the calculation details are described in our publications [7,22–26]. The validity of calculations was proven for the oxidative addition of hydrogen to the square-planar complex $NiCl_2(PH_3)_2$ with d^8 electronic configuration of the central atom [25,26]. A good agreement of calculations with experimental data allowed us to

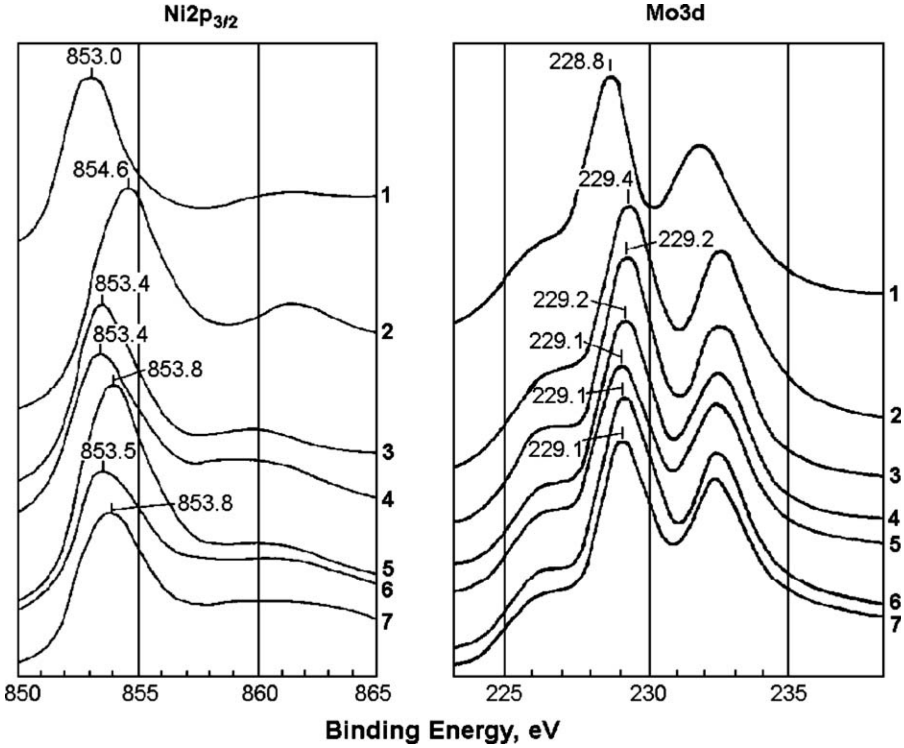

Fig. 3. XPS data on the electronic state of Ni and Mo in the active component composition of the sulfide (Ni,Mo)/Sibunit catalysts. (1) NiS/Al_2O_3 catalyst and mechanical mixture (MoS_2 + Al_2O_3); (2) (Ni,Mo)/Sibunit catalyst sulfided *ex situ* at 400 °C; (3) the previous sample is evacuated *in situ* at 400 °C until residual pressure of 5×10^{-9} Torr; (4) the previous sample is reduced *in situ* in hydrogen at 300 °C; (5) the previous sample is sulfided *in situ* in (H_2 + H_2S) at 300 °C; (6) the previous sample is evacuated *in situ* at 300 °C until residual pressure of 5×10^{-9} Torr; and (7) the previous sample is sulfided *in situ* in (H_2 + H_2S) at 300 °C. (Taken from [6].)

use the same quantum-chemical methods for the analysis of the electronic state of Ni and Co within the active component of sulfide catalysts.

Calculations were carried out for the Ni(Co)$Mo_2S_{10}H_{10}$ cluster, which has the following characteristic features [7,22]:

- This cluster is a fragment of the active component's structure, the interatomic distances in which were found experimentally with EXAFS [27–29].
- The Ni (Co) atom is located at the vertex of a square pyramid formed by four sulfur atoms; the pyramid height is 0.5 Å [27–29] (Figs. 4 and 5).
- The stoichiometry of this cluster differs from MoS_2, but the calculated charges on Mo and S are "stoichiometric" due to the compensation of the free valence bonds of sulfur atoms by terminal hydrogen atoms [30].

Dissociative adsorption of a hydrogen molecule on Ni atom within the active component results in the formation of a complex containing an adsorbed (H_s) and an occluded (H_o) hydrogen atom (see Fig. 4) and in a considerable decrease in the calculated energy of the system ($\Delta E = -46.0$ kcal/mol). The optimized interatomic distances Ni–H_s and Ni–H_o are 1.43 and 1.48 Å, respectively. The calculated formal charge on these atoms suggests that surface hydrogen H_s is more "acidic" ($q = +0.16$) than occluded hydrogen H_o ($q = -0.42$). The oxidative addition of a hydrogen molecule results in a considerable increase in the formal charge on nickel (from +0.45 to +0.79) due to the covalent binding of Ni ion to the sulfur ions in the pyramid base. Two important circumstances should be emphasized in this connection:

1. The electron density is partially transferred from the nickel atoms to the sulfur atoms bound to them rather than to the molybdenum atoms as one could expect; this result is in good agreement with XPS data (see the previous section).
2. The d_{z2} and d_{xy} orbitals of nickel (in the coordinate system used in Fig. 4) become formally "vacant" and, as shown below, it is these orbitals that participate in the adsorption of donor molecules.

A similar situation is observed in the oxidative addition of hydrogen to Co(II) ion within the active component (Fig. 5). The calculated thermodynamic probability of the formation of surface and occluded hydrogen has shown that the total decrease in the free energy is approximately the same for both cases as shown in Fig. 5. Therefore, it can be stated with a high degree of certainty that if hydrogen adsorption is possible, so its occlusion into the active component matrix should occur with the same probability.

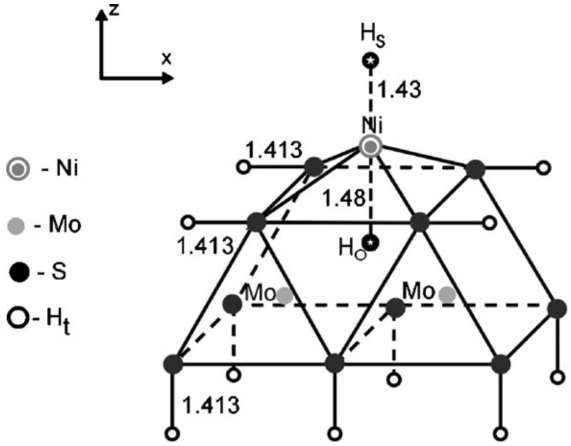

Fig. 4. Quantum-chemical model of the $NiMo_2S_{10}H_{10}$ cluster after oxidative addition of a hydrogen molecule to a Ni atom (the bond lengths are indicated in Å) [26].

The optimized interatomic distances Co–H_o and Co–H_s are 1.52 and 1.42 Å, respectively.

Apparently, the only experimental proof of existence of occluded hydrogen is the hexagonal layered disulfide $H_{0.76}NbS_2$, which crystallizes in the molybdenite structural type [32,33]. The neutron diffraction method was used to study the structure of a single crystal of this disulfide and to determine the hydrogen atom coordinates [33]. The latter indicate that hydrogen atom is situated in the center of an "empty" trigonal prism formed by six sulfur atoms. It was found that the hydrogen atom is located in the center of the triangle formed by niobium atoms with Nb–S distance being 1.93 Å (Table 1). As follows from Table 1, the structure of niobium disulfide undergoes minor changes upon hydrogen occlusion: the unit cell volume and the interatomic distances Nb–Nb and Nb–S increase slightly. This proves that atomic hydrogen introduced in the center of an "empty" trigonal prism does not distort the disulfide structure.

Indirect experimental evidence of the occluded hydrogen existence can be shortly summarized as follows.

1. High quantity of hydrogen retained by bulk MoS_2 and WS_2 after adsorption of hydrogen at elevated temperature [34–38]. This amount exceeds considerably the monolayer coverage.
2. Hydrogen is strongly bound with both bulk and supported MoS_2 and WS_2 and can be removed at temperature as high as 400 °C, i.e. at temperature that is higher than typical catalytic reactions. If Co (or Ni) is introduced into disulfide, the temperature of hydrogen evolution shifts to high value [39–43].

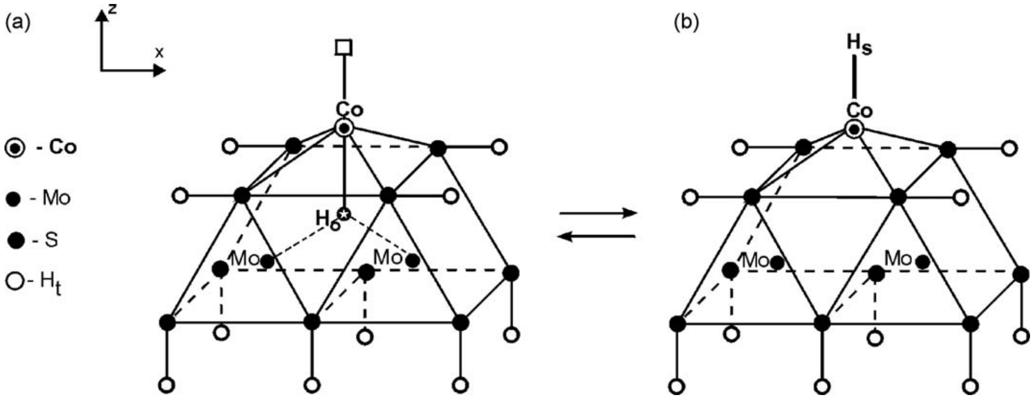

Fig. 5. Quantum-chemical model of an (H)$CoMo_2S_{10}H_{10}$ cluster. The active site is Co(III) ion in the d^6 electronic configuration in the sulfide Co/MoS_2 catalyst with the occluded (a) and adsorbed (b) hydrogen. □, a vacant coordination site.

Table 1
Crystallographic data on the structure of the hexagonal NbS_2 with and without occluded hydrogen.

System	NbS_2 [31]	$H_{0.76}NbS_2$ [32]	MoS_2 [33]
Space group	$P6_3/mmc–D^4{}_{6h}$	$P6_3/mmc$	$P6_3/mmc–D^4{}_{6h}$
Structure	Hexagonal	Hexagonal	Hexagonal
Volume ($Å^3$)	114.02	119.7	
$a = b$ (Å)	3.320 (1)	3.34 (7)	3.1602 (1)
c (Å)	11.945 (4)	12.39 (5)	12.294 (4)
Nb–H (Å)		1.928 (6)	
S–H (Å)		2.51 (1)	
N–S (Å)	2.467	2.51 (1)	2.42
Nb–Nb (Å)	3.320	3.34 (7)	3.16

The corresponding parameters of hexagonal single crystal of molybdenum disulfide are shown for comparison.

3. One can obtain one and the same sulfide catalyst which contains and does not contain strongly bounded hydrogen [44].
4. Analysis of the literature data on the fundamental vibration frequencies of hydrogen in sulfide catalysts made in [3,4] has shown that some of them can be assigned to the occluded hydrogen. These vibration frequencies coincide very well with frequencies calculated for the occluded hydrogen in our models [5,7,8].

5. Concerted mechanism of C–S bond hydrogenolysis

There are two independent and mutually exclusive concepts of the mechanism of hydrodesulfurization, which are being developed simultaneously. In one of them, it is assumed that the decisive role in the mechanism of catalysis by metal sulfides belongs to the bond energy of surface sulfur atoms with the solid catalysts, which determines the ability for creation of anion vacancies – active sites of the sulfide catalysts. The other one, which is being developed at the G.K. Boreskov Institute of Catalysis, is based on the common nature of heterogeneous, homogeneous and enzyme catalysis as a natural phenomenon. The first concept of mechanism is reviewed in details in [3,4], here we will consider the second concept in relation to the Lewis acid–base catalysis.

Concerted (synchronous) mechanisms play a key role in enzyme catalysis. Publications on homogeneous and heterogeneous catalysis in which the concerted mechanism of catalytic transformations is also assumed appear currently with increasing frequency [19–21]. For Brønsted acid–base reactions, such catalytic transformations are possible if the acidic and basic sites of the catalyst act in a concerted way, provided that they are sufficiently close to each other and are oriented strictly in such a way that the substrate coordination becomes favorable for catalysis. In such a case, the high rate of catalytic transformation is ensured by synchronous proton transfer along a system of chemical and hydrogen bonds in cyclic intermediate structures. There are also examples of concerted mechanisms in heterogeneous catalysis involving molecular oxygen [45–48]. Concerted mechanisms are characterized by low activation energy (E_a) and high process selectivity.

The main relationships of thiophene hydrogenolysis on sulfide catalysts have been considered in details in reviews [15,49]. Here we note just the most important specific features of this reaction:

1. Hydrogenolysis of thiophene on bimetallic sulfide catalysts is characterized by low activation energy 7–14 kcal/mol even for low active Ni–Nb, Ni–Re, Cu–W, etc. catalysts.
2. The thiophene hydrogenolysis reaction is characterized by high selectivity: four hydrogen molecules are added at once to one thiophene molecule, so, no products of partial hydrogenation or hydrogenolysis of thiophene ring (butadiene, in particular) appear in the gas phase.

As noted above, the active component of sulfide hydrodesulfurization catalysts is an electrically neutral macromolecule $(MoS_2)_x$ with Ni(IV) or Co(III) ions in the d^6 configuration located in its edge plane. A fragment of this macromolecule in real scale with allowance for all interatomic distances and ionic radii is represented in Fig. 6. There is occluded hydrogen inside the macromolecule. It reacts with Ni or Co surface atoms, creating electronic configuration of the active metal required for adsorption and catalysis. Under catalysis conditions, the active site always contains an adsorbed hydrogen sulfide molecule; this favors stabilization of the “active state” of nickel or cobalt [7,26].

The Co(III) or Ni(IV) atoms in the d^6 electronic configuration within the active component of HDS catalysts have two “empty” $3d_{z2}$ and $3d_{xy}$ orbitals due to oxidative addition of hydrogen (Fig. 7). Hence, they are strong Lewis acid centers which can effectively interact with a lone electron pair of a hydrogen sulfide

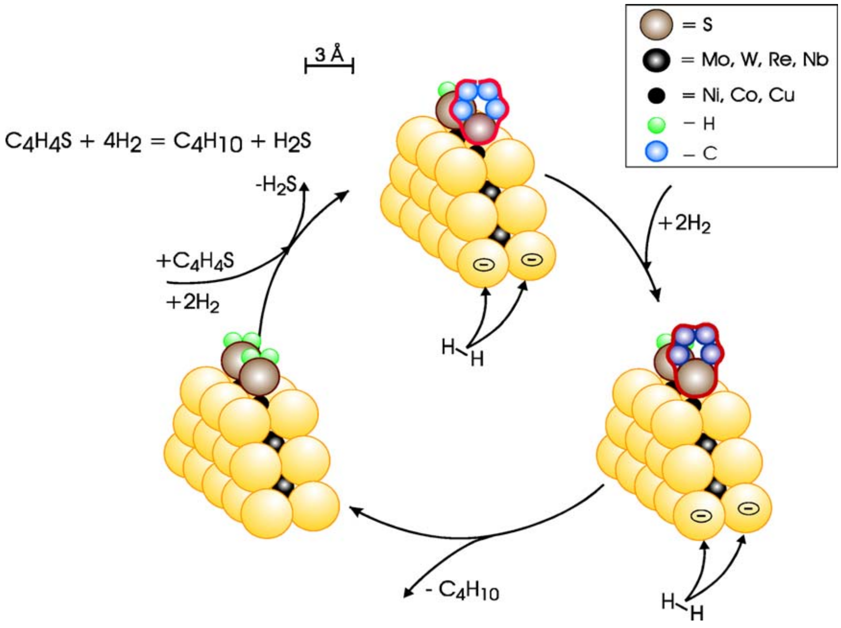

Fig. 6. The catalytic cycle of thiophene hydrogenolysis on the sulfide bimetallic species – active component of the HDS catalysts.

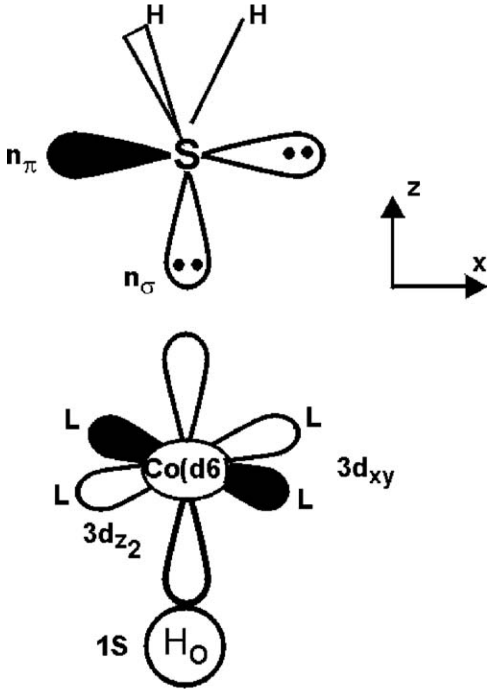

Fig. 7. Scheme of interaction of $n\sigma$ and $n\pi$ orbitals of a hydrogen sulfide molecule with $3d_{z2}$ and $3d_{xy}$ orbitals of the Co(III) atoms in the d^6 electronic configuration.

molecule to form a chemical bond M–S. This bond is rather weak (Table 2) that means chemisorption of a molecule. Heat of thiophene adsorption on the active metal is twice higher in comparison with hydrogen sulfide (Table 2). Therefore, the catalytic cycle of thiophene hydrogenolysis starts with supplanting hydrogen sulfide from the coordination sphere of the active component by a thiophene molecule (Fig. 6). As was shown in [51], the electron density from sulfur atom of thiophene transfers to a MoS_2 macromolecule after η^1-coordination of thiophene to Mo atom at the edge plane and this charge is completely delocalized in the macromolecule so that the process cannot be taken as a local one. Obviously, this process can also occur if the thiophene molecule is coordinated to an active metal (Co,Ni) in the SBMS composition. In such a case, an additional negative charge appears on the electrically neutral macromolecule of the active component. Since all valence bonds inside a macromolecule are saturated, the excess negative charge could be localized on the terminal sulfur atoms.

Let us now consider the activation of molecular hydrogen by sulfide catalysts. The activation of molecular hydrogen can occur either as a result of its oxidative addition or homolytic or heterolytic splitting [48]. However, the homolytic activation of a hydrogen molecule on the surface of metallic catalysts can be regarded as a particular case of the hydrogen oxidative addition [17]. Each metal atom in the catalyst bulk is surrounded by neighbors in all directions, while surface atoms possess free coordination sites and can donate electrons to bonding and antibonding orbitals of hydrogen resulting in its dissociation.

In the case of sulfide catalysts, both heterolytic and homolytic activation of hydrogen can occur [52]. The former process can be realized with participation of Mo–S or Ni–S bonds, while the second one may proceed on Mo–Mo or Ni–Ni sites. At the same time, homolytic dissociation of molecular hydrogen on the $(\bar{1}\,0\,1\,0)$ S-edge requires approximately the same activation energy than that on the $(1\,0\,\bar{1}\,0)$ metal edge [53]. To our mind, a homolytic dissociation of hydrogen can proceed at the edge plane of S atoms in the following way. Edge planes of a single slab of an electro-neutral macromolecule MoS_2 are restricted by either $(1\,0\,\bar{1}\,0)$ plane of sulfur atoms or $(3\,0\,\bar{3}\,0)$ plane of Mo atoms (Fig. 8). For the first time, the surface structure of ionic crystals which can be obtained by cleavage of stoichiometric crystals was considered in detail by Farragher [54]. In our case, an electro-neutrality principle can be formulated as follows. For a MoS_2 macromolecule of any size, a MoS_2 stoichiometry must be strictly maintained and the sum of broken bonds on surface sulfur atoms must be equal to the sum of broken bonds on Mo atoms. However, the edge planes of stoichiometric and regular hexagonal macromolecule are slightly relaxed towards interatomic distances inside macromolecule [55,56]. According to [56], Mo^1–Mo^1 distance increases, but Mo^1–Mo^2 decreases in relation to Mo^1–Mo^3 and Mo^3–Mo^3 distances (Fig. 8). The broken valence bonds of peripheral sulfur atoms S^1 can participate in the formation of pairwise S–S bonds resulting in its shortening [56]. The presence of disulfide groups $(S–S)^{2-}$ in bulk MoS_2 is indicative by a characteristic band at 529 cm^{-1} in the Raman spectra [57].

Binuclear molybdenum clusters $[(C_5H_5)Mo(\mu\text{-}S)_2(\mu\text{-}S_2)]_2$ with bridging disulfide groups [58,59] can serve as a good model for studying the dissociative adsorption of the hydrogen molecule on terminal sulfur atoms:

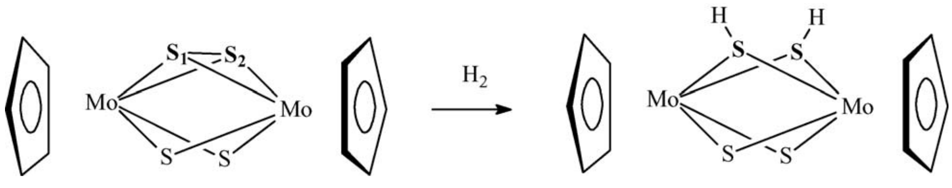

Table 2
Heats of adsorption of hydrogen sulfide, thiophene and tetrahydrothiophene (THT) on the active sites of different composition.

Method of calculation	Composition of active component	Heat of adsorption (kcal/mol)			Reference
		H_2S	Thiophene	THT	
Interacting bonds	Co/MoS_2	11.5	21.2	35.1	[50]
	Ni/MoS_2	12.2	22.1	36.0	
	Co/WS_2	11.9	21.7	35.8	
	Ni/WS_2	12.6	22.6	36.8	
Hartree–Fock	Co/MoS_2	16.5	18.4	26.7	[7]

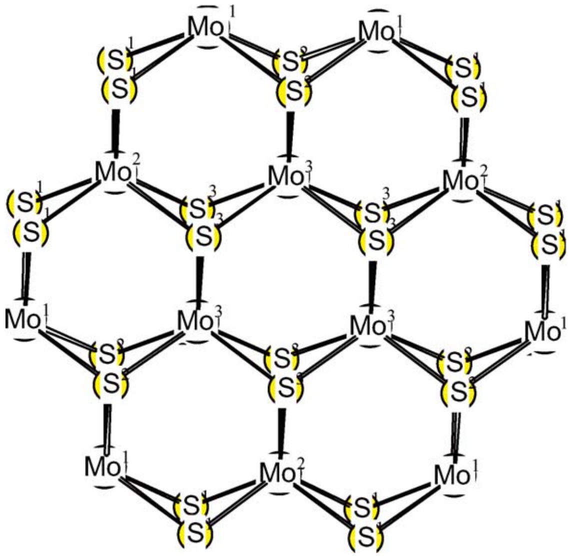

Fig. 8. Electro-neutral macromolecule of MoS_2 ($Mo_{12}S_{24}$).

Thus, terminal sulfur atoms in the edge plane of the MoS_2 single slab can be regarded as Lewis basic centers which can donate electron density to the hydrogen molecule resulting in its dissociation and formation of new chemical bonds S–H. The activated hydrogen is transferred through the system of chemical bonds created by bridging sulfur atoms to the adsorbed thiophene molecule (Fig. 6). This process results in thiophene hydrogenation and in the removal of π-conjugation of the thiophene ring. The tetrahydrothiophene (THT) molecule, which is more basic than the thiophene molecule, remains strongly bound to the active site (Table 2) [50]. After hydrogenation of thiophene ring, a pair of electrons participating in the formation of aromatic ring of thiophene is transferred through the THT sulfur atom to the macromolecule of the active component. Again, this excess of negative charge becomes the driving force of dissociative hydrogen adsorption. The activated hydrogen formed due to dissociation is transferred back to the adsorbed THT molecule through the system of chemical bonds. This results in the rupture of C–S bond, liberation of butane to the gas phase and formation of adsorbed hydrogen sulfide. An adsorbed H_2S molecule, which is a weak ligand, can be replaced again by a thiophene molecule. The catalytic cycle is thus closed.

The concerted mechanism of thiophene hydrogenolysis considered here cannot be attributed to redox reactions, because it does not explicitly assume reduction and reoxidation of the sulfide catalyst surface during the catalytic cycle.

6. Conclusion

Sulfide catalysts of hydrotreating of oil fractions constitute one of the best-studied and thoroughly characterized systems in heterogeneous catalysis. The success in the studies of these catalysts was considerably favored by the specific structure of their active component [60–62]. Therefore, the knowledge of the structure of the active component of these catalysts offers wide opportunities for the understanding of the fundamentals of the nature of the catalytic action of sulfide catalysts.

Below the main specific features of the concerted mechanism of thiophene hydrogenolysis on sulfide hydrodesulfurization catalysts are formulated.

1. The chemical reaction occurs in the coordination sphere of the bimetallic sulfide active component without participation of structure-forming sulfur atoms in the catalytic cycle.
2. An indispensable part of the active site consists of an occluded hydrogen atom that appears in the active component due to oxidative addition of hydrogen to Ni(II) or Co(II) during the catalyst sulfidation. The occluded hydrogen is located in the matrix of a MoS_2 single slab in the center of an “empty” trigonal prism formed by six sulfur atoms under a nickel (cobalt) atom at the distance of 1.5 Å from it. The occluded hydrogen creates an electronic configuration of Ni (Co) essential for activation of the thiophene molecule.
3. The active sites of thiophene activation consist of Ni(IV) or Co(III) atoms in the d^6 electronic configuration, which are the Lewis acids. Adsorption occurs due to the donation of the unshared electron pair of sulfur atoms of substrate to vacant d_{z2} and d_{xy} orbitals of the active metal atom.
4. The activation of hydrogen occurs on the couplet sulfur atoms at the edge planes of a single MoS_2 (WS_2) slab. The driving force of this process is the presence of the S–S chemical bond at the terminal sulfur atoms that restrict an electrically neutral macromolecule of the active component and act as the Lewis basic sites. The excess of electron density is transferred from these atoms to the antibonding orbital of a hydrogen molecule, which results in its homolytic dissociation.
5. The high rate of catalytic transformation is ensured by the fast transfer of electrons and protons along the system of chemical bonds within an electrically neutral macromolecule of the active component.
6. The low activation energy of chemical transformation is explained by the high degree of energy compensation required for the cleavage of “old” bonds in a thiophene molecule by the energy released in exothermic processes of adsorption and hydrogenation of the thiophene ring.
7. The concerted mechanism of thiophene hydrogenolysis on sulfide HDS catalysts relates to the class of acid–base heterogeneous catalytic reactions.
8. The concerted mechanism is also applicable to other sulfide catalysts that are crystallized in the molybdenite structural type.

Probably, concerted (synchronous) mechanisms of catalytic processes apply to a wider range of heterogeneous catalysts than was believed until recently. The main difficulty in revealing such mechanisms consists in the non-uniform composition of the surface species in the real heterogeneous catalysts, which can catalyze the given catalytic transformation in different directions. This complicates considerably the analysis of kinetic regularities and makes it necessary to build complex kinetic models. Obviously, the solution of this problem is based on the creation of heterogeneous catalysts with homogeneous composition and with a known structure of the active component.

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