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Sulfide hydrodesulfurisation catalysts: structure of the active component and mechanism of the catalytic action

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Abstract. A new phenomenon in heterogeneous catalysis, namely, oxidative addition of hydrogen to active metal atoms (Ni, Co) within sulfide hydrodesulfurisation catalysts, is considered. The possibility of hydrogen occlusion into the MoS_2 matrix of the active components of these catalysts is demonstrated. The electronic structure of Ni(IV) and Co(III) active sites with d^6 electronic configuration is analysed. The concerted mechanism of thiophene hydrogenolysis on a bimetallic active site is considered and substantiated. The concept of the governing role of the metal–sulfur bond energy in catalysis by metal sulfides is analysed critically. The bibliography includes 198 references.

I. Introduction

Hydrotreating of oil fractions is the largest-scale process in the petroleum refining industry. Over 80 million barrels of oil (about 12.7 million m^3) are processed in the world daily; the average sulfur content in this oil being 1.0 mass % – 1.3 mass %.[1] In the last decade, the requirements for the quality of motor and jet fuels have increased considerably due to deterioration of the environmental conditions. According to the EC Directive of 11.05.2001, the total content of sulfur in diesel fuel should not exceed 50 ppm by 2005, whereas the content of aromatic compounds should not exceed 10 vol.%. The existing industrial hydrotreating catalysts only ensure a decrease in the sulfur content to $\sim$ 500 ppm in diesel fuel; the required level can be achieved by either increasing the process temperature by 38 °C,[2] or decreasing considerably the liquid hourly space velocity of the feed stock, or, finally, enhancing considerably the activities of catalysts. The latter variant is the most cost-effective because the contribution of the catalyst cost to the production cost of the hydrotreating product is less than 0.5%. Therefore, world leading laboratories pay much attention to the development of new-generation catalysts for the deep hydrotreating of oil fractions. This can be illustrated by the fact that the range of hydrotreating catalysts includes more than 200 trade names.[3]

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In this review, we will not dwell on the methods for catalysts' preparation, their chemical compositions, porous structures, kinetic studies of the hydrotreating process, *etc*. The issues of catalytic hydrotreatment of oil fractions are probably considered in most detail in the monograph by Topsøe *et al*.;[4] the problems of deep hydrotreating, in the review by Vasudevan and Fierro;[5] specific features of hydrogenolysis of polyaromatic sulfur-containing compounds, in the paper by Whitehurst *et al*.;[6] and certain technological problems are analysed in the paper by Furimsky.[7]

The main purpose of this review is to analyse the fundamental aspects of hydrogenolysis of the C – S bond on sulfide hydrotreating catalysts. A decade has passed since the publication of the previous review on this subject.[8] Considerable progress in understanding the mechanism of action of sulfide catalysts at the molecular level has been made during this period. Generally speaking, establishing the mechanism of heterogeneous catalysis and the nature of chemical interaction of reactants with solid catalyst surfaces is a very difficult task. This originates from the following reasons:

— as a rule, several types of compounds differing in composition and structure are present on a catalyst surface; as a result, chemical transformations occur in various directions and pathways to give diverse intermediates and side products in the gas phase;

— the degree of surface coverage by adsorbed molecules can vary over a very broad range, which complicates kinetic studies;

— in the overwhelming majority of cases, the structures of active sites on solid catalysts are unknown; therefore, certain theoretical models of the active component have to be used, based on analogies with the known structures [in this sense, sulfide hydrotreating catalysts present a rare exception: the geometric structures of their active components have been studied rather thoroughly (see below)];

— until now, there has been a lack of sufficiently sensitive physical methods (similar to multinuclear NMR in homogeneous catalysis) that would enable *in situ* studies of adsorption and chemical transformations of molecules on a surface;

— as a rule, heterogeneous catalytic reactions occur under drastic conditions (at high temperatures and pressures) where the reaction medium can affect the structure of the active component.

It is only the chemical and phase compositions of a catalyst that are usually known, and the structure of the active component is determined using a number of physical, chemical and kinetic methods in order to obtain responses of the catalytic system to various external impacts. Subsequently, correlations between the catalyst's activity and selectivity, on the one hand, and some

specific parameter, on the other, are plotted and general features of a given chemical reaction are revealed.

There are two independent and mutually exclusive concepts of the mechanism of hydrodesulfurisation 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 catalyst. The other one, which is being developed at the G K Boreskov Institute of Catalysis, is based on the concept of the common nature of heterogeneous, homogeneous and enzyme catalysis as a natural phenomenon. The present review is devoted to the consideration of these concepts.

II. The structure of the active component of sulfide catalysts of hydrodesulfurisation

1. The geometric structure of the active component

Industrial catalytic hydrotreating of oil fractions began in the middle of the 1950s because of the necessity of preparation of gasoline fractions for the reforming process. In turn, reforming served as a source of inexpensive hydrogen required for hydrotreating. Hydrotreating was initially performed on a composition of sulfide compounds of two metal pairs, *viz*., Mo(W)–Ni(Co). These catalysts were used in coal liquefaction which was developed in Germany in the middle of the 1930s. Until now, they remain unsurpassed and possess the best combination of operational properties,[9] *viz*., activity, stability, resistance against poisons, cost, *etc*., though intense searches for new catalytic systems were carried out throughout all these years.

The accumulation of experimental data on the general regularities of hydrogenolysis of the C–S bond on these catalysts favoured the appearance in the 1950s–1960s of the first model of the structure of the active component;[10] it was called the 'monolayer' model.[11] Later, this model was improved [12,13] taking into account the inevitable sulfidation of the catalyst under the working conditions.

In parallel with the monolayer model, other models based on concepts of the sulfide forms of the MoS_2 and WS_2 catalysts appeared and were developed; these include intercalation models [14–16] and models with spatially separated MoS_2 and Co_9S_8 clusters.[17] A special place is occupied by models of surface complexes and boundary grains proposed by Phillips and Fote.[18]

The appearance in the 1960s of new methods for the study of highly dispersed species in supported catalysts opened prospects for more detailed studies of the active component of hydrodesulfurisation catalysts. This led to new models suggesting that bimetallic sulfides are the active components.[19,20] The model known as 'synergism upon contact' was transformed into the 'long-range control' model.[21] We believe that the most attractive model is that proposed by Ratnasamy and Sivasanker.[22] It assumes that 'promoter' atoms, *viz*., Co or Ni, are added to free valence bonds of the S atoms at the MoS_2 edge plane. However, this viewpoint did not receive convincing experimental confirmation; therefore, other models were created later (in the 1980s) based on the concept of a single MoS_2 slab† with Co ions incorporated at the edge plane.

Probably, the model of 'Co–Mo–S phase' developed by Topsøe *et al*.[4] was recognised as the best; it assumed the localisation of Co ions at the edge plane of a single MoS_2 slab. This model was based on results of a Mössbauer emission spectroscopic study of catalysts, which was later confirmed by EXAFS data. Subsequently, this model was developed by other authors.[23–27] The similarity of the structures of MoS_2 and the Co–Mo–S phase is undoubted, but there are at least three viewpoints on the localisation of the Co(Ni) ions. For example, Nieman *et al*.[28] assume that Co or Ni atoms have a square-planar coordination of sulfur atoms located at the $(10\bar{1}0)$ edge of a single MoS_2 slab. Bouwens *et al*.[29] believe that a square-pyramidal surrounding of five sulfur atoms at the edges of a single MoS_2 slab is characteristic of Co, whereas Ledoux *et al*.[30] proposed distorted tetrahedral and octahedral coordinations for them (which followed from data obtained by ^{59}Co NMR).

An essentially similar model called 'SBMS' (sulfide bimetallic species) has been developed at the G K Boreskov Institute of Catalysis.[8,31–35] Using modern physicochemical methods for studies of solid catalyst surfaces, it was shown that an SBMS consists of a single $MoS_2(WS_2)$ slab with Ni(Co) atoms at its $(10\bar{1}0)$ edge plane. Figure 1 shows the structure of an SBMS active complex with an occluded hydrogen atom. The Ni(Co) atoms are coordinated to four sulfur atoms of the MoS_2 matrix, while the fifth coordination site is occupied by an adsorbed H_2S molecule. In such a case, the Ni(Co) atom is located in the centre of a square pyramid of sulfur atoms (the distance from the base plane to the Ni(Co) atom is 0.5 Å). The occluded hydrogen atom is located in the centre of an 'empty' trigonal prism of the MoS_2 sulfide matrix at a distance of 1.5 Å under the Ni(Co) atom.

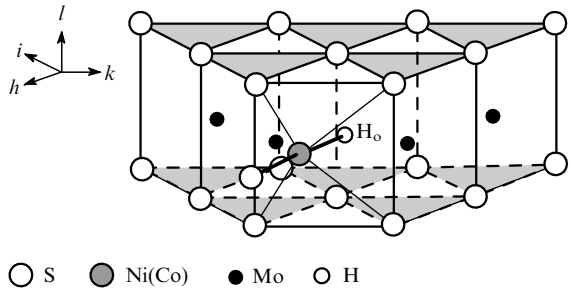


Figure 1. Structure of the active component of sulfide hydrodesulfurisation catalysts with an occluded hydrogen atom.
The bases of the trigonal prisms made of sulfur atoms, in the centres of which molybdenum atoms are located, are cross-hatched.

The SBMS model differs from other similar models in a number of points which we believe to be fundamental; they are listed below.

1. The necessary and sufficient structural element in SBMS consists of a single slab of MoS_2 (or some other disulfide that crystallises according to the molybdenite structural type) with ions of a transition metal (nickel, cobalt or any other metal that can interact with the sulfide matrix) situated at its edge plane. These ions are the catalyst active sites. This structure is also found in bimetallic sulfides 'Ni–W–S', 'Cu–W–S', 'Ni–Nb–S', 'Ni–Re–S', *etc*., whose matrices crystallise according to the molybdenite (MoS_2) structural type.[31]

2. Hydrogen occluded during the catalyst sulfidation step is the second essential element of SBMS. It is hydrogen that defines the electronic structure of the active metal atom. The SBMS model does not make distinction between the square-planar and square-pyramidal coordination of active metal ions; these two states are transformed into each other once occluded hydrogen and adsorbed hydrogen sulfide have been eliminated.

3. The bimetallic sulfide species is an electrically neutral macromolecule.

4. The SBMS sizes on the surfaces of various supports in the most active catalysts do not exceed 10–20 Å, which means that no separate phase of this compound exists (in the crystallographic sense). Only the MoS_2 or WS_2 phase is detected by diffraction methods.

† A single MoS_2 slab is a sandwich in which a layer of molybdenum atoms is arranged between two layers of sulfur atoms, so that a molybdenum atom is located in the centre of a trigonal prism of sulfur atoms and every second prism remains 'empty'.

The SBMS model was developed using highly active sulfide catalysts obtained by the synthesis of the corresponding metal-complex precursors on supports of differing nature (Al_2O_3, SiO_2, a new carbon material Sibunit) followed by their conversion to the sulfide form.[36,37] The catalysts prepared by this method had uniform chemical compositions. This made it possible to obtain more reliable information about the structure of the active component and about the electronic state of the constituent metal ions. The following methods were used to study the structure of the active component: high-resolution transmission electron microscopy (HRTEM),[38] X-ray photoelectron spectroscopy (XPS),[39] X-ray radial atomic distribution,[40] EXAFS.[41] In all the cases (except XPS, as explained below), the results obtained are in good agreement with the available literature data; therefore, we have the right to state that synthesis of catalysts from metal-complex precursors provides the same structure of the active component as that in catalysts prepared by traditional methods. On the other hand, the higher activity of the catalysts obtained from metal-complex precursors in comparison with those prepared by traditional methods demonstrates the superiority of systems with uniform composition of surface compounds. It can be expected that in this case all the supported metal is involved in the active component and participates in the catalytic reaction.

2. The electronic structure of the active component

The electronic structure of the transition metal atom (or ion) is a key factor determining the catalytic activity of sulfide catalysts. It is the metal electronic structure and the ligands surrounding it that determine its ability to adsorb a substrate molecule. However, the electronic structure of metal atoms in the active component of sulfide catalysts has not been considered in the literature. This stems from the complexity of the system in question and the absence of adequate models describing the state of active metal atoms.

X-Ray photoelectron spectroscopy is a main method for the study of the electronic state of metals in supported catalysts. Numerous XPS studies of complex compounds of metals with organic and inorganic ligands showed[42] that the binding energy (E_b) of electrons on the central atom levels is a complex function of the metal oxidation state, coordination state and the nature of atoms involved in the first coordination sphere. The metal – metal chemical bond can also contribute significantly to this dependence. Nevertheless, E_b can characterise the metal oxidation state or its formal charge provided that the first coordination sphere of the metal is the same. However, studies of solid catalysts inevitably involve a number of experimental difficulties in the determination of this magnitude, as described in sufficient detail in reviews.[43,44]

XPS was also used to study the electronic state of metals in sulfide catalysts.[45–49] Different types of catalytic systems were studied, including bulk catalysts and catalysts on oxide (Al_2O_3, SiO_2) and carbon (Sibunit) supports, at different steps of genesis. While the results regarding the state of Mo (or W) ions are in most cases consistent with data on bulk MoS_2 and WS_2 samples, the state of Co (or Ni) ions is a matter of discussion.[4] This is primarily due to the non-uniform composition of surface compounds which results in broadening of XPS spectral lines.

Shortly after we started studies on sulfide catalysts prepared from organometallic precursors, we obtained quite an unexpected result:[39] the $Ni2p_{3/2}$ line turned out to be shifted by 1 eV towards higher binding energies in comparison with the similar line of highly dispersed nickel sulfide, which suggested an increase in the oxidation state of the Ni atom. Later, this result was reproduced with remarkable permanency for many systems, including both bulk systems[50] and those supported on alumina.[51] Opponents asked a reasonable question: considering that nickel (or cobalt) should be reduced to lower oxidation states at high temperatures in a hydrogen environment, how is it possible that you observe the opposite phenomenon?

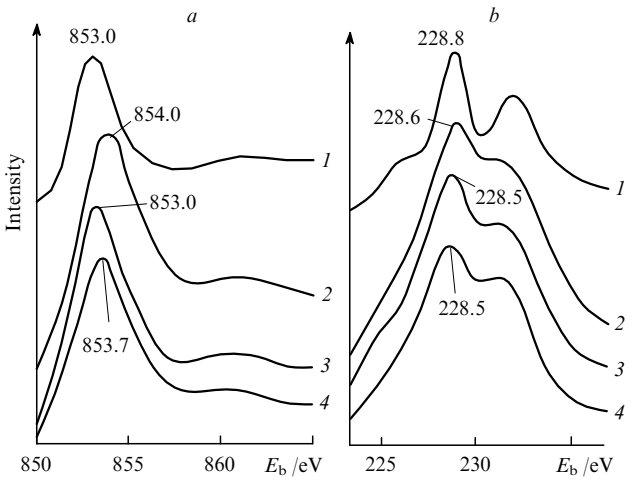


Figure 2. Electronic states of $Ni2p_{3/2}$ (*a*) and Mo3d (*b*) atoms within the active component of sulfide catalysts $(Ni,Mo)S_x/Al_2O_3$ according to XPS data.[52,53]

(*1*) Highly dispersed NiS/Al_2O_3 catalyst (*a*) and $MoS_2 + Al_2O_3$ mechanical mixture (*b*); (*2*) $(Ni,Mo)S_x/Al_2O_3$ catalyst sulfided *ex situ* in a stream of H_2S at 400 °C; (*3*) sample *2* preheated *in vacuo* at 300 °C to a residual pressure of 5×10^{-9} Torr; (*4*) sample *3* sulfided *in situ* in an $H_2 + H_2S$ mixture at 300 °C.

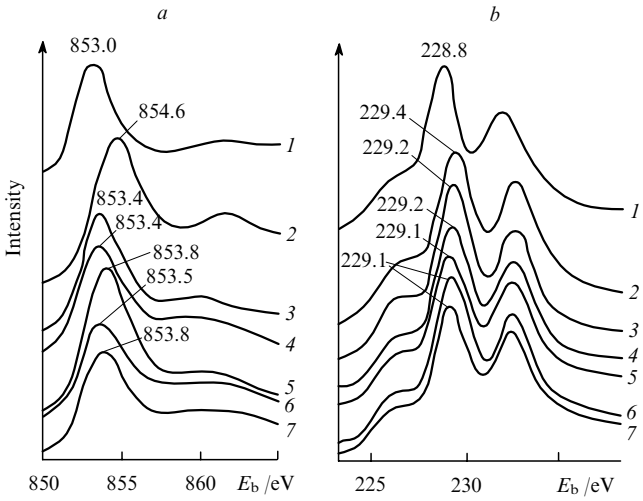


Figure 3. Electronic states of $Ni2p_{3/2}$ (*a*) and Mo3d (*b*) atoms within the active component of sulfide catalysts $(Ni,Mo)S_x$/Sibunit according to XPS data.[52,53]

(*1*) Highly dispersed NiS/Sibunit catalyst (*a*) and mechanical mixture MoS_2 + Sibunit (*b*); (*2*) $(Ni,Mo)S_x$/Sibunit catalyst sulfided *ex situ* in a stream of H_2S at 400 °C; (*3*) sample *2* preheated *in vacuo* at 300 °C to a residual pressure of 5×10^{-9} Torr; (*4*) sample *3* treated with hydrogen at 300 °C; (*5*) sample *4* sulfided *in situ* in an $H_2 + H_2S$ mixture at 300 °C; (*6*) sample *5* preheated *in vacuo* at 400 °C to a residual pressure of 5×10^{-9} Torr; (*7*) sample *6* sulfided *in situ* in an $H_2 + H_2S$ mixture at 300 °C.

We undertook a special study to answer this question using *in situ* XPS for sulfide (Ni,Mo)-catalysts‡ supported on alumina and Sibunit.[52,53] Catalysts sulfided *ex situ* were placed in the chamber of an XPS spectrometer without contact with air. The Mo3d line in the spectra of $(Ni,Mo)S_x/Al_2O_3$ sulfide catalysts is a narrow, poorly resolved doublet. The E_b ($Mo3d_{5/2}$) value matches similar values for bulk and highly dispersed MoS_2 (Fig. 2). In the spectra of bimetallic sulfide catalysts supported on Sibunit, this line is represented by a narrow, well-resolved doublet (Fig. 3) shifted

‡ The catalysts were obtained using metal complex precursors.

towards higher E_b values (in comparison with similar values for the bulk and highly dispersed MoS_2) due to epitaxial interaction of the active component with the surface of the conducting carbon material. It should be noted that the position of this line in the spectra of both catalysts did not change upon their thermal treatment in the spectrometer chamber (see Figs 2 and 3).

The situation with the Ni2p line is quite different. In the spectra of catalysts supported on alumina (see Fig. 2), the $Ni2p_{3/2}$ line is rather narrow and is shifted by 1 eV towards higher E_b values in comparison with the spectrum of highly dispersed NiS. This shift is even more significant in the spectra of catalysts supported on Sibunit (see Fig. 3). After thermal treatment of sulfide catalysts in high vacuum at 300–400 °C, the $Ni2p_{3/2}$ line shifts back towards lower binding energies so that its new position corresponds to a formal charge of 2+ on the nickel atom in highly dispersed NiS. If the sample is sulfided again in the spectrometer chamber, this line is shifted back to higher E_b values (see Figs 2 and 3). The reversible shift of the Ni2p line (see Fig. 3) implies that resulfidation reverts the catalyst to its original state.

When studying solid catalysts by XPS, the changes in the binding energies of electrons on inner levels of the atom of interest are often related to the impossibility of relaxation of the energy accumulated in dispersed species upon their photoionisation (see *e.g.*, Refs 54 and 55). However, at least four counterarguments can be offered against this interpretation of results for the given catalytic system.

1. The NiS species in catalysts supported on Al_2O_3 are no larger than 10 Å (see Ref. 56). Thermal treatment of such catalysts in the chamber of an XPS spectrometer first in high vacuum and then in hydrogen actually reduces the sulfide species to the metal. It is very important that heating of reduced catalysts in an $H_2 + H_2S$ mixture does not result in the re-formation of sulfide species.[53]

2. Thermal treatment of sulfide catalysts in the spectrometer chamber under various conditions does not change the position of the Mo3d line, whereas the position of the Ni2p line changes significantly and reversibly. Had the relaxation effect existed, similar changes in E_b would be expected for both metals.

3. An increase in E_b is also observed for bulk catalysts Ni–MoS_2 (Ni–WS_2),[50] in which the nickel atoms are situated at the edge planes of the bulk disulfide.

4. The carbon support Sibunit is a conducting material, which excludes 'charging' of a sample under ionising irradiation.

These arguments allow us to state that the reversible change in the E_b of electrons on the inner levels of nickel cannot be explained by any physical effect of irradiation on the object being studied. It should be interpreted as a chemical phenomenon, namely, the increase in the binding energy of electrons on the inner levels of nickel (or cobalt) should be ascribed to an unusually high oxidation state of nickel within the active component of sulfide hydrodesulfurisation catalysts.

Let us try to explain why our data disagree with those obtained by other authors who studied similar systems. First, as noted above, sulfide catalysts synthesised from metal-complex precursors are characterised by high uniformity of the composition of surface species; as a result, the XPS lines become rather narrow. Second, these effects are not observed if sulfide catalysts have been exposed to air for a long time, as it is quite obvious that oxidation processes can occur in this case. It should be noted that results obtained by other researchers in experiments that took all the possible unfavourable effects into account (see, *e.g.*, Ref. 57) are in good agreement with our data.

The possibility of existence of Ni(IV) ions with the d^6 electronic configuration was confirmed by *ab initio* theoretical studies of the $Ni(S_2C_2H_2)_2$ and $Ni(S_2C_2H_2)_2(H_2S)$ complexes.[58–60] The results obtained show that the square planar complex $Ni^{II}(S_2C_2H_2)_2$ with the d^8 electronic configuration[61] is converted to a square-pyramidal Ni(IV) complex with the d^6 configuration upon adsorption of an H_2S molecule on the fifth coordination position. This is accompanied by the displacement of the nickel atom by 0.35 Å from the plane of the four sulfur atoms. Similar conversion occurs upon adsorption of H_2S on active Ni sites within the active component. In this case, the electron density is transferred from nickel atoms to the neighbouring sulfur atoms bound to nickel, rather than to the molybdenum atom. It should be noted that this conclusion agrees with the XPS data (see Figs 2 and 3).

To explain the unusually high oxidation state of Ni, we assumed the possibility of the oxidative addition of hydrogen to a nickel ion within the active component.[52,62,63] *Ab initio* calculations confirmed that the oxidative addition of hydrogen accompanied by the formation of Ni(IV) with the d^6 electronic configuration is thermodynamically favourable. It is assumed that a hydrogen molecule adds to a Ni(II) ion in a dissociative way to give a 'surface' hydrogen atom (H_s) and an 'occluded' hydrogen atom (H_o). The latter is localised in the matrix of the active component under the nickel atom, in the centre of an 'empty' trigonal prism formed by six sulfur atoms (see Fig. 1).

The concept of the oxidative addition of hydrogen to the nickel atom within the active component allows us to explain the XPS data presented above. In fact, *ex situ* evacuation of a sulfided sample at elevated temperature should remove occluded hydrogen due to reductive elimination to give Ni(II). Treatment with an $H_2 + H_2S$ mixture results in the oxidative addition of hydrogen; as a result, the Ni2p line is displaced towards higher binding energies. Prolonged exposure of samples to air can result in the oxidation of occluded hydrogen.

The first compound containing Ni(IV) ions was obtained more than 90 years ago.[64] It was the heteropolymolybdate anion $[NiMo_9O_{32}]^{6-}$. It is important for the existence of nickel in the high oxidation state that the number and electronegativity of the ligands surrounding the nickel atom be sufficiently high. The Ni(IV) cation in the complex mentioned above is located in a pseudo-octahedral coordination of oxygen atoms and has a d^6 electronic configuration. All the known Ni(IV) complexes are diamagnetic and tend to have an octahedral coordination.[65,66] Of other Ni(IV) compounds, the following inorganic compounds deserve mentioning: K_2NiF_6, $BaNiO_3$, NiO_2, $NaNiIO_6$, $NiAs_2$, *etc*. (see Ref. 67).

3. Substantiation of the possibility of oxidative addition of hydrogen in heterogeneous catalysis

Since at present there are no direct experimental methods for studying the nature of transient species formed upon adsorption of the starting reagents on the sites of heterogeneous catalysts, we will refer to analogies in the structures and mechanisms of action of homogeneous catalysts in order to explain the possibility of oxidative addition of hydrogen to these sites, although the conditions of the corresponding processes (temperature, pressure, presence of a solvent) differ considerably. Our approach is based on the concept of the common nature of the homogeneous, heterogeneous and enzyme catalysis.[68–71]

The oxidative addition of hydrogen to square-planar Ir(I) complexes was discovered over 40 years ago[72] and is now one of the key reactions in homogeneous catalysis.[73] In particular, it is well known that this reaction is the first step in the formation of active sites on catalysts for alkene hydrogenation.[74] In such a case, hydrogen acts as a unique molecule that simultaneously displays both reducing and oxidising properties under the same catalytic reaction conditions.

The oxidative addition of hydrogen is a particular case of the addition of neutral molecules XY to transition metal compounds with free coordination centres. The molecule XY is reduced in this reaction to give two anionic ligands X^- and Y^-, whereas the metal is oxidised. One of the examples best known is the oxidative addition of hydrocarbons R–H to complexes of M(0) metals discovered by Shilov;[75,76] this reaction is accompanied by an increase in the formal oxidation state of the metal by two units and formation of alkyl hydride complexes. Since alkyl and hydride

ligands are very strong reducing agents, stable reaction products contain metals in low oxidation states only.

Numerous examples of the oxidative addition of hydrogen to various transition metals are currently known.[73] Two types of oxidative addition of hydrogen, *viz*., two- and single-electron addition, are distinguished. In the study mentioned above,[72] the oxidative addition of hydrogen resulted in the formal transformation of Ir(I) (d^8 electronic configuration) into Ir(III) (d^6 configuration):

$$(PH_3)_2Ir^{I}(CO)Cl + H_2 \longrightarrow (PH_3)_2Ir^{III}(CO)ClH_2.$$

The addition of hydrogen to metals in higher oxidation states, *e.g*., to Os(II), is also known:[77]

$$(PH_3)_2Os^{II}Cl_2 + H_2 \longrightarrow (PH_3)_2Os^{IV}Cl_2H_2,$$

$$Os^{II}(d^6) \longrightarrow Os^{IV}(d^4).$$

The oxidative addition of hydrogen can also involve Group VI metals, *e.g*., Mo(II):[78]

$$(PH_3)_2Mo^{II}Cl_2 + H_2 \longrightarrow (PH_3)_2Mo^{IV}Cl_2H_2,$$

$$Mo^{II}(d^4) \longrightarrow Mo^{IV}(d^2).$$

A typical example of the two-electron hydrogen addition to square-planar complexes is the synthesis of the Wilkinson catalysts:[79]

$$RhCl(PPh_3)_3 + H_2 \longrightarrow RhH_2Cl(PPh_3)_3.$$

It is important to note that the oxidative addition occurs readily if the coordination sphere of the metal comprises donor molecules such as PPh_3, PBu_3 and the like. In the reactions considered above, the formal oxidation state of the metal and its coordination number increase by two units. Examples of the single-electron oxidative addition of hydrogen, *e.g*., to Co(II) [$Co^{II}(d^7) \longrightarrow Co^{III}(d^6)$], are also known.[80, 81]

$$2\,Co^{II}(CN)_5^{3-} + H_2 \rightleftharpoons 2\,HCo^{III}(CN)_5^{3-},$$

$$2\,Co^{II}(dmgH) + H_2 \rightleftharpoons 2\,HCo^{III}(dmgH)$$

dmg is dimethylglyoxime.

The latter reaction is typical of square-planar complexes that have a pronounced tendency towards oxidative addition.

Because the possibility of oxidative addition of hydrogen to an active metal atom within the active component of sulfide catalysts was only shown by non-empirical quantum-chemical methods, it was desirable to confirm the validity of this conclusion for known structures. The square-planar complex $NiCl_2(PH_3)_2$ with the d^8 electronic configuration of the central atom was selected for this purpose.[62] The calculation details are described in our publications.[58–60, 62, 63]

In this kind of theoretical calculations, the change in the system free energy upon formation of a new chemical compound is the main validity criterion. For example, a theoretical study[82] showed that the oxidative addition of hydrogen to the structural analogues $PtCl_2(PH_3)_2$ and $PdCl_2(PH_3)_2$ results in an energy decrease (ΔE) by -32.2 and -67.8 kJ mol^{-1}, respectively. In the reaction

$$Ni^{II}Cl_2(PH_3)_2 + H_2 \longrightarrow Ni^{IV}H_2Cl_2(PH_3)_2$$

the ΔE value was found to be -52.4 kJ mol^{-1} (see Refs 61 and 62). The geometric structure of the complex obtained was optimised totally; the interatomic distances and bond angles are shown in Fig. 4.

The electronic state of nickel on transition from a square-planar $Ni^{II}(d^8)$ complex to an octahedral $Ni^{IV}(d^6)$ complex is shown in a correlation diagram (Fig. 5). As follows from the calculations, the oxidative addition of hydrogen results in a considerable destabilisation of the nickel d_{z^2} orbital, whereas the

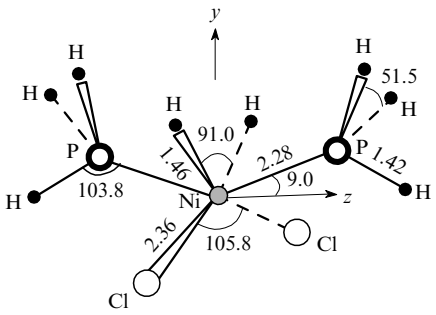


Figure 4. Geometric structure of the d^6 complex $Ni^{IV}H_2Cl_2(PH_3)_2$ totally optimised at the MP2 level (C_{2v} symmetry).[63] The bond lengths and angles are specified in angstroms and degrees, respectively.

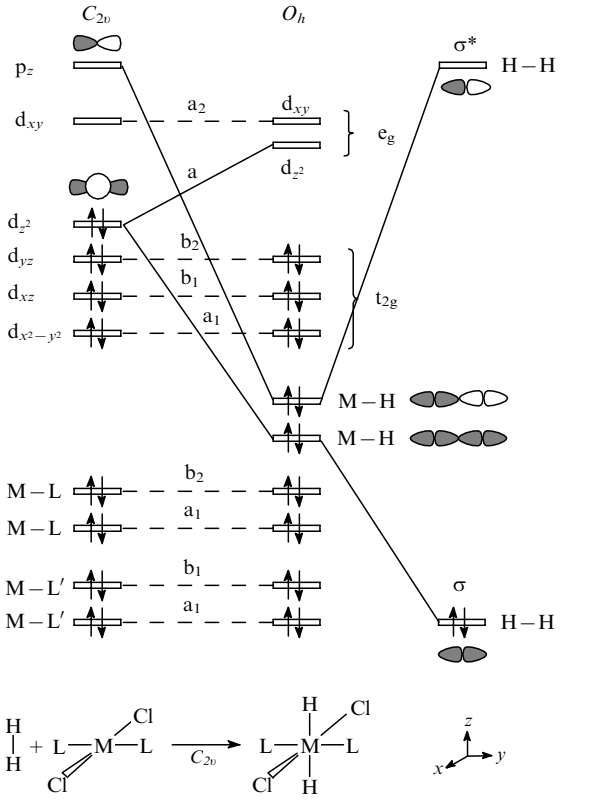


Figure 5. Correlation diagram of oxidative addition of hydrogen to the square-planar complex $Ni^{II}Cl_2(PH_3)_2$ in the d^8 electronic configuration.[65] The coordinate of the $H_2 + M(d^8)L_2Cl_2 \rightarrow M(d^6)L_2Cl_2H_2$ reaction maintains the C_{2v} symmetry.

4p orbital stabilises due to the formation of a Ni – H bond. Thus, the d_{xy} and d_{z^2} orbitals become formally vacant, whereas the electron density on the Ni4s and Ni4p orbitals increases. The binding energy of electrons on the Ni2p level was calculated using this correlation diagram.[63] It was found to be 1.5 eV lower for Ni(II) than for Ni(IV). This result agrees very well with experimental results for nickel metal complexes[83] and with X-ray photoelectron spectra of sulfide catalysts.[39, 50–53, 57]

Such a good agreement allowed us to use the same quantum-chemical methods for the analysis of the electronic states of nickel and cobalt 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:[63, 84]

(1) this cluster is a fragment of the active component's structure, the interatomic distances in which were found experimentally by EXAFS;[85–87]

(2) 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 [85–87] (Figs 6 and 7);

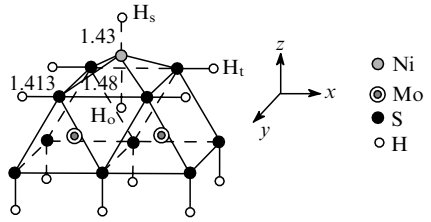


Figure 6. Quantum-chemical model of the $NiMo_2S_{10}H_{10}$ cluster after oxidative addition of a hydrogen molecule to a nickel atom (the bond lengths are indicated in Å).[63]

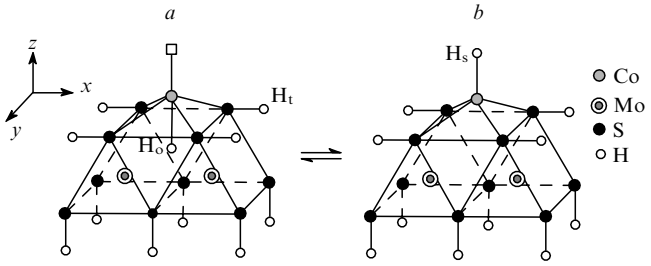


Figure 7. Quantum-chemical model of an $(H)CoMo_2S_{10}H_{10}$ cluster [the active site is Co(III) in the d^6 electronic configuration] in Co/MoS_2 catalyst with occluded (*a*) and adsorbed (*b*) hydrogen.
□ — vacant coordination site.

(3) 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.[88]

Non-empirical calculations were carried out using the Gaussian 92 quantum-chemical computational complex [89] at the Hartree–Fock method (HF), the Müller–Plesset perturbation theory (MP2) and the density functional theory (DFT) levels.

Dissociative adsorption of a hydrogen molecule on nickel atoms 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. 6) and in a considerable decrease in the calculated energy of the system ($\Delta E = -192.9$ kJ mol^{-1}). The optimised interatomic distances Ni–H_s and Ni–H_o are 1.43 and 1.48 Å, respectively. The calculated formal charges on these atoms suggest 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 nickel ions to the sulfur ions in the pyramid base. Two important circumstances should be emphasised 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_{z^2} and d_{xy} orbitals of nickel (in the coordinate system used in Fig. 6) 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) ions within the active component (see Fig. 7). Zakharov and Startsev [84] calculated the thermodynamic probability of the formation of surface and occluded hydrogen. *Ab initio* calculations showed that the total decrease in the free energy is approximately the same in both cases shown in Fig. 7; therefore, it can be stated with a high degree of certainty that if hydrogen adsorption is possible, then its occlusion into the active component matrix should occur with the same probability. The optimised interatomic distances Co–H_o and Co–H_s are 1.52 and 1.42 Å, respectively.

It follows from *ab initio* calculations that an important role in the stabilisation of the electronic state of Ni(IV) and Co(III) within the active component belongs to the hydrogen sulfide molecule adsorbed on the active metal atom. The interaction scheme of the orbitals of a donor H_2S molecule with vacant orbitals of Co(III) is presented in Fig. 8 [this scheme also applies to Ni(IV)]. The calculated heats of adsorption of hydrogen sulfide on Ni and Co sites are 82.6 and 69.6 kJ mol^{-1}, respectively,[67,84] whereas the heat of adsorption of hydrogen sulfide on Ni(II) is as small as 36.0 kJ mol^{-1} (see Ref. 67). Due to the difference in the heats of adsorption of the H_2S molecule on Ni(II) and Ni(IV) sites, the equilibrium bond lengths Ni^{II}–S and Ni^{IV}–S are different (2.77 and 2.60 Å, respectively).[67]

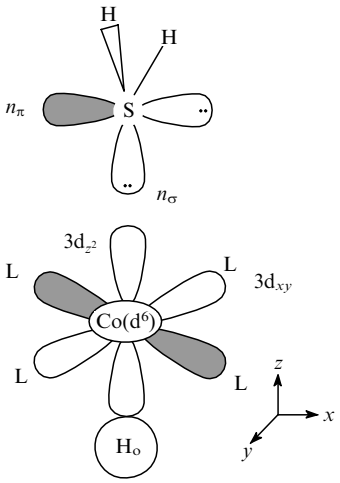


Figure 8. Scheme of interaction of n_σ and n_π orbitals of a hydrogen sulfide molecule with $3d_{z^2}$ and $3d_{xy}$ orbitals of the Co(III) atom in the d^6 electronic configuration.

4. Experimental proof of the existence of occluded hydrogen

Since direct experimental proof of the existence of occluded hydrogen is absent in the literature, let us try to analyse numerous data available on the $MoS_2 + H_2$ system in order to obtain information about the state of hydrogen in this system. We will pay attention to whether or not particular experimental data are consistent with the concept of the existence of occluded hydrogen.

The considerable adsorption of hydrogen by bulk molybdenum disulfide was probably first noted by Badger *et al.*[90] At 140 °C and 1 atm, the quantity of hydrogen retained by the sample is 0.37 mol of H_2 per mol of MoS_2, which is much higher than that corresponding to the monolayer coverage. It was shown [91–94] that the quantity of hydrogen adsorbed by bulk MoS_2 and WS_2 at 300–400 °C is at least three times higher than that in the case of monolayer coverage (the latter was measured using the adsorption of N_2 and CO_2). If MoS_2 is supported on alumina, the quantity of adsorbed hydrogen increases considerably.[95–98] Since the layered packing of molybdenum disulfide is irregular in this case, Jalowiecki *et al.*[96,97] assumed that spillover of hydrogen from MoS_2 to the surface of the support occurs. The latter serves as a 'reservoir for hydrogen storage'.[97] Some other aspects of hydrogen sorption by bulk and supported molybdenum sulfide were described in a review by Moyes.[99]

However, the existence of 'excessive' hydrogen in sulfide catalysts can also be explained from a different standpoint. Let us consider the strength of hydrogen binding to catalysts, which can easily be evaluated from the temperature at which hydrogen appears in the gas phase during the temperature-programmed heating (TPH) of catalysts. Erofeev and Kaletchits [100, 101] were the first to discover strongly bound hydrogen which was desorbed from Co–Mo sulfide catalysts at temperatures above 400 °C. Hoodless *et al.*[102] showed the presence of both weakly and strongly bound hydrogen in bulk MoS_2 (the total hydrogen content corresponded to the formula $H_{0.027}MoS_2$). If cobalt was introduced in a MoS_2 sample, the peak of hydrogen evolution shifted towards higher temperatures; at the optimum catalyst composition, the maximum hydrogen desorption was observed at 600 °C (the hydrogen content in the catalysts corresponded to the formula $H_{0.015}Co_{0.8}MoS_2$). Similar results were later obtained by other authors.[103–107]

We undertook a study of the forms of hydrogen desorption from sulfide catalysts in the TPH mode (Fig. 9).[108] The catalysts were prepared by supporting metal-complex precursors on alumina followed by sulfidation of the samples in a stream of H_2S at 400 °C. There are two regions in which hydrogen is removed from all the catalysts studied: a low-temperature region (desorption temperatures up to 500 °C) and a high-temperature region. Weakly bound hydrogen is removed in the low-temperature region, whereas strongly bound hydrogen is removed in the high-temperature region. After removal of hydrogen from the catalysts in the TPH mode at temperatures up to 750 °C, the samples were again sulfided portionwise with H_2S at 400 °C and re-desorption was carried out in the TPH mode (see Fig. 9, curves *2*). It was found that re-sulfided samples did not contain strongly bound hydrogen.

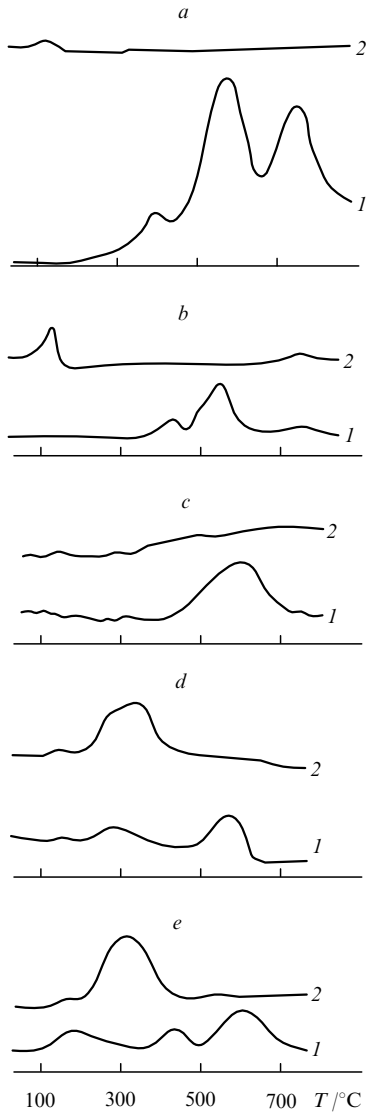


Figure 9. Desorption of hydrogen from sulfide catalysts.[108]
(*1*) Catalysts sulfided *in situ* in a stream of H_2S at 400 °C; (*2*) the same samples sulfided after TPH with portions of H_2S at 400 °C. Catalysts: (*a*) 3.0 Co/Al_2O_3, (*b*) 3.0 Ni/Al_2O_3, (*c*) 7.1 Mo/Al_2O_3, (*d*) (1.6 Co + 7.5 Mo)/Al_2O_3, (*e*) (1.6 Ni + 7.1 Mo)/Al_2O_3.

We believe that the strongly bound hydrogen is the hydrogen occluded in the sulfide matrix. In fact, every second trigonal prism built of sulfur atoms in the structure of molybdenum disulfide (see Figs 1 and 10) is 'empty'. If we subtract the ionic radius of S^{2-} (1.58 Å) from the interatomic distance Mo–S (2.41 Å), we obtain the radius of the 'empty' space (0.83 Å), which is slightly longer than the H–H distance in the hydrogen molecule (0.74 Å). Thus, the introduction of a hydrogen atom or even a hydrogen molecule into this space will not distort the structure of molybdenum disulfide. *Ab initio* calculations of the active component structure with an occluded hydrogen atom showed [62, 84] that the optimised interatomic distances Ni–H_o (1.48 Å) and Co–H_o (1.52 Å) correspond to covalent binding. It is easy to show that these 'optimised' distances coincide with those calculated from the geometric structure of molybdenum disulfide.

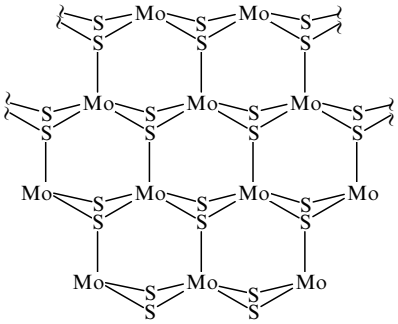


Figure 10. An electrically neutral $(MoS_2)_x$ macromolecule.

The term 'occluded hydrogen' § in relation to sulfide catalysts was introduced because of the necessity to emphasise its specific role in the formation and functioning of the active component. Let us note the most important properties of occluded hydrogen:

(1) strong bonding to the active component matrix (occluded hydrogen is removed only at temperatures much higher than those of typical catalytic reactions);

(2) localisation only on specific sites of the active component matrix [unlike dissolved (absorbed) hydrogen];

(3) interaction with surface metal atoms, owing to which occluded hydrogen favours the creation of an 'active' electronic configuration of these atoms (it is this configuration that determines the catalytic and adsorption properties of the active component);

(4) oxidative properties (occluded hydrogen appears due to the oxidative addition of hydrogen to an active metal atom at the step of formation of the active component and therefore plays the role of an oxidant).

Hexagonal layered disulfide $H_{0.76}NbS_2$, which crystallises in the molybdenite structural type (Table 1), is one of the few

§ Occlusio (Latin) means locking, hiding; occlude (English) — to close, seal. In metallurgy, the term 'occlusion' means dissolution of gases in solid or molten metals. In chemistry, there are synonyms for this word: absorption and dissolution.

Table 1. Crystallographic data on the structure of hexagonal NbS_2 with and without occluded hydrogen. The corresponding parameters of hexagonal single-crystal MoS_2 are shown for comparison.

System	Space group	Unit cell parameters /Å		Volume /Å^3	Bond lengths /Å				Ref.
		$a = b$	c		M–H	S–H	M–S	M–M	
NbS_2	$P6_3/mmc$ (D^4_{6h})	3.320(1)	11.945(4)	114.02	–	–	2.467	3.320	109
$H_{0.76}NbS_2$	$P6_3/mmc$	3.34(7)	12.39(5)	119.7	1.928(6)	2.51(1)	2.51(1)	3.34(7)	110
MoS_2	$P6_3/mmc$ (D^4_{6h})	3.1602(1)	12.294(4)	–	–	–	2.42	3.16	111

systems where the presence of occluded hydrogen has been proved experimentally.[109–111] The neutron diffraction method was used to study the structure of a single crystal of this disulfide and to determine the hydrogen atom coordinates.[110] The latter indicate that this atom is situated in the centre of an 'empty' trigonal prism formed by six sulfur atoms. It was found that the hydrogen atom is located in the centre of the triangle formed by niobium atoms (the Nb–H distances are ~1.93 Å). One can see from Table 1 that the structure of niobium disulfide[109] undergoes minor changes upon hydrogen occlusion: the unit cell volume and the interatomic distances Nb–S and Nb–Nb increase slightly. This proves that atomic hydrogen introduced in the centre of an 'empty' trigonal prism does not distort the structure of the disulfide. Similar results, albeit with less unambiguous conclusions, were previously obtained by the same research group[112] for the H_xTaS_2 system.

Let us compare the vibration frequencies of occluded hydrogen calculated by non-empirical methods with literature data obtained by different spectroscopic methods (Table 2). The stretching vibrations of the S–H bonds in H_xMoS_2 lie in the region 2450–2650 cm^{-1} (see Ref. 113), which corresponds to the similar parameters for pure compounds containing thiol groups.[114] Inelastic neutron scattering (INS) spectra of a $H_{0.5}TaS_2$ sample contained[112] a band at 744 cm^{-1}, which was assigned to the deformation vibrations of the Ta–S–H group. It was concluded that this compound was non-stoichiometric covalent tantalum hydrosulfide. However, the absence of bands of the stretching vibrations of the S–H bonds casts doubt on the validity of this assignment. A similar band was found by Wright and co-workers[110] in the spectra of an $H_{0.76}NbS_2$ sample. Of the three possible variants of assigning this band, deformation vibrations of the Nb–H bond in the direction parallel to axis c were preferred. The INS method was later used to study the H_xMoS_2 and H_xWS_2 systems.[91–94] The absence of structural data for these systems made Wright and co-workers be very careful when

Table 2. Fundamental vibration frequencies of hydrogen in sulfide catalysts and their assignments (literature data).

Catalyst	Spectroscopic method[a]	Hydrogen adsorption conditions	Vibration frequencies /cm^{-1}	Assignment	Ref.
H_xMoS_2	IR	200 °C	2516 (broad)	–	113
		200 °C with subsequent evacuation at 300 °C	2649	–	
			2532	ν_{S-H}[b]	
			2454	–	
$H_{0.5}TaS_2$	INS	electrochemical reduction	744	δ_{Ta-S-H}[c]	112
$H_{0.76}NbS_2$	INS	the same	2600	–	110
			1544	–	
			744	δ_{Nb_3-H}	
H_xWS_2	INS	400 °C	2659	ν_{S-H}	94
			2470	ν_{S-H}	
			694	δ_{S-H}	
$H_{0.067}MoS_2$	INS	300 °C, 0.9 atm	1977	–	91
			1348	–	
			847	–	
			662	–	
H_xMoS_2	INS	room temperature, 1 atm	872	δ_{Mo-S-H}, δ_{Mo-H}	92
			662	δ_{S-H}	
		room temperature, 70 atm[d]	872	δ_{Mo-S-H}, δ_{Mo-H}	
			662	δ_{S-H}	
			~400	?	
H_xMoS_2/Al_2O_3	INS	300 °C, 0.9 atm	960	–	91
			686	–	
			400	–	
H_xNiMoS_2	INS	adsorption at 1–30 atm, desorption *in vacuo* at 200–400 °C	1895	ν_{Ni-H}	115
			795	?	
			650	δ_{S-H}	
H_xCoMoS_2	CNS	$H_2 + H_2S$, then H_2 at 800 °C	1392 ± 26	–	116

[a] INS is inelastic neutron scattering, CNS is Compton neutron scattering. [b] The vibration frequencies of the S–H bond in gaseous H_2S, thiophene and thiols are 2668, 2550 and 2550–2650 cm^{-1}, respectively (see Ref. 114). [c] The stretching vibration bands of the S–H bonds are absent. [d] The results obtained were interpreted as evidence of activated adsorption and formation of intercalated hydrogen.

assigning the observed absorption bands. However, they noted the following facts: (1) treatment of sulfide catalysts with hydrogen at 300 – 400 °C resulted in the appearance of bands corresponding to the stretching vibrations of the S—H bonds, whereas these bonds were not observed at low temperatures; (2) the bands at ~870 and ~660 cm^{-1} were observed in the spectra of samples which did not contain bands corresponding to the stretching vibrations of the S—H bonds, hence they should be assigned to other types of vibration [*e.g.*, the former band may be assigned to the deformation vibrations of the M—H bond, whereas the latter, to the deformation vibrations of the H—S_3 bond (vibrations of the hydrogen atom located in the centre of the triangle of S atoms) within the molybdenum disulfide matrix].

Anderson *et al.*[117] employed the semiempirical molecular orbital method ASED-MO ¶ to calculate the vibration frequencies of hydrogen in the H_xMoS_2 matrix (Table 3). A comparison of data in Tables 2 and 3 shows that the band around ~870 cm^{-1} can be assigned to the deformation vibrations of occluded hydrogen located in the centre of the triangle of molybdenum atoms, and hence in the centre of the 'empty' trigonal prism of sulfur atoms. The calculated bond length Mo—H (1.82 Å) totally agrees with the structural characteristics of molybdenum disulfide, hence the results obtained may be considered rather reliable.

Table 3. Vibration frequencies of hydrogen in a MoS_2 matrix calculated by the ASED-MO method.[117]

Bond type	Vibration frequency /cm^{-1}	
	stretching	deformation
H—S (basal)	2347	432
H—S (side)	2292	492, 583
H—S (angular)	2190	621
H—Mo^{IV}	1901	519
H—Mo^{II}	1948	224
H—Mo_3 (see [a])	—	865

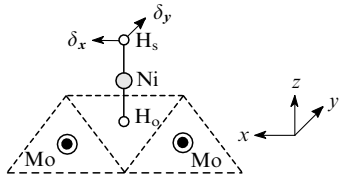
[a] Vertical vibrations of hydrogen in the centre of a triangle of molybdenum atoms.

Very few spectroscopic studies of hydrogen adsorption by bimetallic sulfide catalysts are known. In their meticulous study, Sandberg *et al.*[115] carried out hydrogen adsorption at high pressure; subsequently, the samples were evacuated at 200 – 400 °C and studied using the INS method (see Table 2). Thus, the study was aimed at the 'residual', strongly bound hydrogen which is not removed at temperatures above the catalytic reaction temperature. The band at 650 cm^{-1} was assigned to the deformation vibrations of the S—H groups, although the spectra did not contain bands corresponding to the stretching vibrations of these groups and the preparation conditions of the samples favoured, most likely, the elimination of the SH groups from the surface. The broad band with a maximum at 795 cm^{-1} overlaps the band of stretching vibrations of the S—H bonds and the band of vibrations of hydrogen atoms in Raney nickel (950 cm^{-1}). The second broad band at 1895 cm^{-1} was assigned to the stretching vibrations of the Ni—H bond, although vibrations of hydride bonds in metal complexes have frequencies above 1970 cm^{-1}, and those in Raney nickel are equal to 2070 cm^{-1}.

In order to reveal the nature of hydrogen bonding in Ni – Mo sulfide catalysts, we calculated [62] the frequencies of the stretching and deformation vibrations for adsorbed and occluded hydrogen atoms in the $NiMo_2S_{10}H_{10}$ structure (see Fig. 6). As one can see from Table 4, the band at 1895 cm^{-1} in the INS spectra

¶ Atom Superposition and Electron Delocalisation Molecular Orbital.

Table 4. Vibration frequencies and intensities of adsorbed and occluded hydrogen atoms in the active component of Ni – Mo sulfide catalysts calculated by non-empirical methods.[62]



Vibration	Vibration frequency /cm^{-1}		Intensity (arb. units)
	calculated	found	
ν_z^s	1890.0	1895.0	174.0
ν_z^{as}	2010.0		124.5
$\delta_x(H_s)$	704.0		28.4
$\delta_y(H_s)$	834.0	795.0	45.8
$\delta_x(H_o)$	2062.0		339.2
$\delta_y(H_o)$	926.0		12.9

(see Ref. 115) is in good agreement with the deformation vibrations of the H_o—Ni—H_s fragment, whereas the band at 795 cm^{-1} can be assigned to the deformation vibrations of hydrogen adsorbed on nickel. Thus, the vibration frequencies of adsorbed and occluded hydrogen atoms that we have calculated are in better agreement with experimental data than the assignments made by Sandberg *et al.*[115]

Based on measurements of the mean kinetic energy of hydrogen in Co – Mo sulfide catalysts by Compton neutron scattering,[116] the mean vibration frequency of hydrogen in these catalysts was calculated to be 1392 cm^{-1} (see Table 2). The arithmetic mean frequency of the stretching and deformation vibrations of the S—H bond was found to be 1270 – 1310 cm^{-1}. Based on this, Mitchell *et al.*[116] concluded that hydrogen in these catalysts is bound to sulfur atoms because the M—H_s bond frequencies are much lower (~1100 cm^{-1}).

We calculated the vibration frequencies for adsorbed and occluded hydrogen on Co – Mo sulfide catalysts [84] in the coordinate system shown in Fig. 7. The following results were obtained: for Co—H_s $\nu = 1972$ cm^{-1} and $\delta_x \approx \delta_y = 652$ cm^{-1}; for Co—H_o, $\nu = 1696$ cm^{-1}, $\delta_x = 1764$ cm^{-1} and $\delta_y = 880$ cm^{-1}.

The calculated mean vibration frequency of adsorbed hydrogen in Co—H_s is 1092 cm^{-1} and that of occluded hydrogen in Co—H_o is 1447 cm^{-1}, which also agrees satisfactorily with the reported data.[116]

Thus, the spectral characteristics, considered in this section, of hydrogen in sulfide catalysts do not contradict the hypothesis of the existence of occluded hydrogen in these systems but even confirm it. To prove explicitly the existence of occluded hydrogen, it was necessary to perform directed experimental studies of sulfide catalysts with the same chemical composition and structure, either containing or not containing such hydrogen. The first steps in this direction have already been taken. For example, Shalagina *et al.*[108] were the first to obtain this type of sulfide catalysts.

III. The concerted mechanism of thiophene hydrogenolysis on sulfide catalysts

Synchronous (concerted) 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.[68 – 71] Numerous examples of concerted mechanisms in acid-base reactions were considered in a number of papers.[68, 69, 71] 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

manner that the substrate coordination becomes favourable 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.[118–121] Concerted mechanisms are characterised by low activation energies (E_a) and high process selectivity.

Hydrogenolysis of thiophene on sulfide catalysts is the best-studied reaction involving a concerted mechanism.

The main regularities of thiophene hydrogenolysis on bimetallic sulfide catalysts have been considered in detail in a number of reviews;[8, 31–35] let us note just the most important specific features of this reaction.

1. Hydrogenolysis of thiophene on bimetallic sulfide catalysts is characterised by low activation energies, *viz*., 42–63 kJ mol^{-1} in the temperature range 300–400 °C. Modification of catalysts with phosphorus or fluorine decreases the E_a value to 30 kJ mol^{-1}. Even for sulfide catalysts with non-optimum chemical composition (Ni–Nb, Ni–Re, Cu–W) where the reaction rates are low, the E_a values for different metal pairs also range within 38–63 kJ mol^{-1}.

2. The thiophene hydrogenolysis on bimetallic sulfide catalysts with any chemical composition is characterised by high selectivity: four hydrogen molecules are added at once to one thiophene molecule, so, no products of partial hydrogenation of the thiophene ring (in particular, butadiene) appear in the gas phase. Butenes are the only real intermediates; the fraction of butenes in the resulting mixture with butane is the lower the higher the catalyst activity.

These two features serve as a weighty argument that the thiophene hydrogenolysis mechanism should be concerted. Below we describe the mechanism that we suggested for the activation of hydrogen and thiophene molecules and for the transfer of activated hydrogen to an adsorbed thiophene molecule.

1. The mechanism of activation of molecular hydrogen on sulfide catalysts

Hydrogen is the main 'character' in all processes of hydrotreatment of oil fractions; however, there are very few studies on the mechanism of its activation on sulfide catalysts. As a rule, the authors confine themselves to general guesswork without a theoretical substantiation of the interaction of hydrogen with sulfide catalyst surfaces. This happens because few appropriate physicochemical methods are available for *in situ* studies of the adsorption and activation of hydrogen on real catalysts and under real process conditions. On the other hand, the hydrogen activation mechanism has been studied rather thoroughly in homogeneous catalysis. Our subsequent consideration will be based on the concept that the nature of heterogeneous catalysis is the same as that of homogeneous catalysis.

The activation of molecular hydrogen can occur either as a result of its oxidative addition or homolytic and heterolytic cleavage.[122] However, the homolytic activation of a hydrogen molecule on the surfaces of metallic catalysts can be regarded as a particular case of the hydrogen oxidative addition.[73] Each metal atom in the catalyst bulk is surrounded by neighbours on all sides, whereas surface atoms possess free coordination places; therefore, the adsorption of molecular hydrogen on the surface is accompanied by its dissociation (Fig. 11). The liberation of energy upon formation of two metal–hydrogen bonds serves as the driving force of the hydrogen addition to the metal. From the chemical viewpoint, this process can formally be represented as

$$2M^0 + H_2 \longrightarrow 2(M^+ - H^-).$$

The thermodynamic parameters of hydrogen activation on metals are listed in Table 5. The change in the free energy upon the homolytic (dissociative) adsorption of a hydrogen molecule on metals at room temperature is $-(25-109)$ kJ mol^{-1}. To estimate whether heterolytic dissociation of molecular hydrogen on sulfide catalysts is thermodynamically possible, we used the available thermochemical data.[123] As follows from Table 5, the change in free energy is $-(34-117)$ kJ mol^{-1} at temperatures within 300–400 °C typical of catalytic reactions. Thus, there is a reason to believe that the heterolytic activation of a hydrogen molecule on sulfide catalysts is as efficient as the homolytic activation on metals.

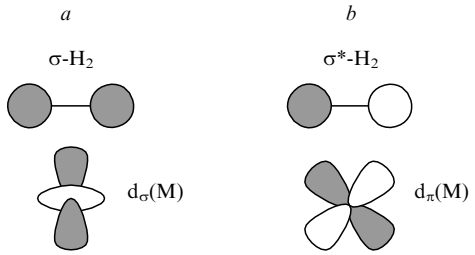


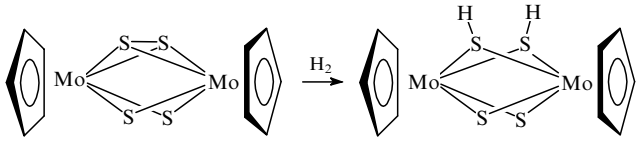
Figure 11. The scheme of interaction between molecular orbitals in the homolytic activation of hydrogen at a metal catalyst surface: (*a*) HOMO, (*b*) LUMO.

Table 5. Some thermodynamic parameters of the activation of a hydrogen molecule on metals and sulfides (a thermochemical estimate).

Parameter	Homolytic activation on metals [122]	Heterolytic activation on sulfide catalysts [123]
Bond energy, H–H /kJ mol^{-1}	436	–
Bond energy, M–H /kJ mol^{-1}	251–293	335–377
Bond energy, S–H /kJ mol^{-1}		210–251
Enthalpy, ΔH° (experimental value) /kJ mol^{-1}	$-(67-151)$	$-(109-456)$
Entropy, ΔS° (estimate) /J mol^{-1} deg^{-1}	-147	-126
$-T\Delta S^\circ$ /kJ mol^{-1}	42 (at 300 K)	75 (at 600 K)
Free energy change, ΔG° /kJ mol^{-1}	$-(25-109)$	$-(34-117)$

However, one should not reject the mechanism of homolytic activation of molecular hydrogen on sulfide catalysts involving terminal sulfur atoms. In fact, it is evident from Fig. 10 that the edges of a single slab of an electrically neutral MoS_2 macromolecule are restricted by either $(10\bar{1}0)$ or $(30\bar{3}0)$ planes. In the former case, the edge is represented by coordinatively unsaturated sulfur atoms; in the latter case, by molybdenum atoms. Taking the principle of electric neutrality into account, it can be stated that free valence bonds of peripheral sulfur atoms can participate in the formation of pairwise S–S bonds, whereas the excess electron density will be delocalised on peripheral molybdenum atoms; these effects can result in the formal 'reduction' of Mo^{4+} into Mo^{2+}. The presence of disulfide groups $(S-S)^{2-}$ in bulk MoS_2 is indicated by the presence of a characteristic band at 529 cm^{-1} in the Raman spectra.[121] The possibility of dissociative (homolytic) activation of hydrogen on terminal disulfide groups was also confirmed by quantum-chemical calculations (see below).

Binuclear molybdenum clusters $(C_5H_5)Mo(\mu\text{-}S)_2(\mu\text{-}S_2)$ with bridging disulfide groups described by Rakowski DuBois [124, 125] can serve as good model compounds for studying the dissociative adsorption of the hydrogen molecule on terminal sulfur atoms.



Molecular hydrogen reacts with disulfide ligands of these complexes under very mild conditions.[124, 125]

The possibility of dissociative adsorption of hydrogen on disulfide ligands was noted in other studies as well.[121, 126] It should be emphasised that a specific role in the interaction with molecular hydrogen belongs to the S–S chemical bond in the disulfide group, since molecular hydrogen does not react with, *e.g.*, sulfur atoms sputtered onto the (110) plane of a molybdenum single crystal.[123, 127]

Thus, molecular hydrogen can be activated on sulfide catalysts according to different mechanisms depending on the catalyst composition and the process conditions. The ease of its activation on sulfide catalysts is indicated by the fact that the isotope exchange H_2-D_2 occurs at 80–150 °C, *i.e.*, at much lower temperatures than the thiophene hydrogenolysis.[128–131] Hence, hydrogen activation cannot limit the overall reaction rate under real hydrotreating conditions.

2. The concerted mechanism of thiophene hydrogenolysis

As noted above, the active component of sulfide hydrodesulfurisation catalysts is an electrically neutral macromolecule $(MoS_2)_x$ with Ni(IV) or Co(III) ions in the d^6 electronic configuration situated at its edge. A fragment of this macromolecule in real scale with allowance for all interatomic distances and ionic radii is represented in Fig. 12. There is occluded hydrogen inside the macromolecule; the former reacts with nickel or cobalt surface atoms, creating the electronic configuration of the active metal atom required for adsorption and catalysis. Under catalysis conditions, the active site always contains an adsorbed hydrogen sulfide molecule; this favours stabilisation of the 'active state' of nickel or cobalt. Adsorption occurs due to efficient interaction between the vacant d_{z^2} and d_{xy} orbitals of the metal atom and the n_σ and n_π orbitals of hydrogen sulfide (see Fig. 8).

The catalytic cycle starts with the displacement of the hydrogen sulfide molecule from the coordination sphere of the active metal atom by a thiophene molecule; this occurs because the heat of adsorption of the latter is higher. The heats of adsorption of

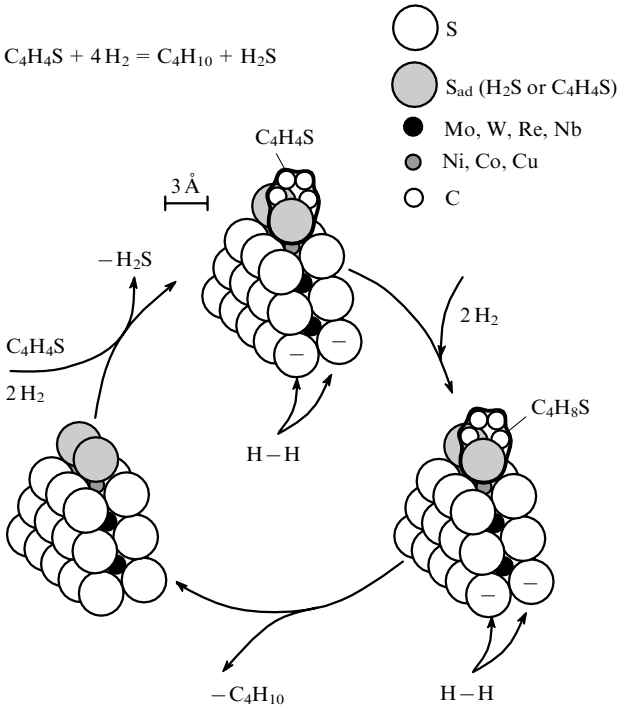


Figure 12. The catalytic cycle of thiophene hydrogenolysis on a bimetallic sulfide compound, *viz.*, the active component of hydrodesulfurisation catalysts [the ratios of interatomic distances and ionic (covalent) radii correspond to actual values].

Table 6. Heats of adsorption of hydrogen sulfide, thiophene and tetrahydrothiophene (THT) on active sites with different compositions.

Calculation method	Composition of the active component	Heat of adsorption /kJ mol^{-1}			Ref.
		H_2S	thiophene	THT	
Method of interacting bonds (MIB)	Co–MoS_2	48	89	147	132
	Ni–MoS_2	51	92	151	
	Co–WS_2	50	91	150	
	Ni–WS_2	53	95	154	
Hartree–Fock method	Co–MoS_2	69	77	112	84

sulfur-containing molecules on active sites with different compositions calculated by semiempirical and nonempirical methods are listed in Table 6.[132] It has been shown[133] that electron density flows from a sulfur atom to a MoS_2 macromolecule if a thiophene molecule is η^1-coordinated with a coordinatively unsaturated molybdenum atom at an edge plane of MoS_2. Obviously, this process can also occur if the thiophene molecule is coordinated with an active metal atom (Co, Ni). In such a case, an additional negative charge appears on the electrically neutral molecule of the active component. Since all valence bonds inside a macromolecule are saturated, the excess negative charge will be localised on the terminal sulfur atoms. In turn, this can become an additional driving force for the dissociative adsorption of the hydrogen molecule by the homolytic activation mechanism according to which electron density is transferred from sulfur atoms to the antibonding orbital of the hydrogen molecule (see the previous section).

The activated hydrogen is transferred through the system of chemical bonds created by bridging sulfur atoms to the adsorbed thiophene molecule, thus providing hydrogenation of the thiophene ring (see Fig. 12). This process results in the removal of π-conjugation from the aromatic thiophene ring and the buildup of additional electron density on the sulfur atom. The tetrahydrothiophene (THT) molecule, which is more basic than the thiophene molecule, remains strongly bound to the active site,[132] whereas the excess electron density is transferred back to the macromolecule of the active component and concentrated on the terminal sulfur atoms. This excess 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 valence bonds. This results in the cleavage of C–S bonds, liberation of butane (butenes) to the gas phase and formation of adsorbed hydrogen sulfide. An adsorbed H_2S molecule, which is a weak ligand, can again be replaced by a thiophene molecule. The catalytic cycle is thus closed.

In order to understand why thiophene is adsorbed and THT is not desorbed during a catalytic cycle, Bulgakov and Startsev[132] used the method of interacting bonds to calculate the heats of adsorption of these molecules on bimetallic sulfide catalysts with different chemical compositions (see Table 6). The low heats of H_2S adsorption imply the considerable reversibility of its adsorption under the catalysis conditions and confirm that adsorbed hydrogen sulfide can be replaced by thiophene. The high heat of THT adsorption completely agrees with the virtual irreversibility of adsorption of this molecule. This also means that the cleavage of C–S bonds and desorption of H_2S and hydrocarbons to the gas phase is the only way to complete the catalytic cycle. The only reason for the strong adsorption of THT on active sites is that the basicity of the sulfur atom in this molecule is higher than that in the thiophene molecule due to the removal of π-conjugation upon hydrogenation of the thiophene ring.

Direct experimental evidence of this mechanism was obtained by EXAFS in an *in situ* study of the adsorption of selenophene (a

structural analogue of thiophene) on $(Ni,Mo)/Al_2O_3$ sulfide catalysts of metal-complex origin.[134] It was shown that the adsorption of selenophene occurs on Ni atoms (the Ni—Se distance is 2.50 Å) but not on Mo atoms.

Thus, adoption of the hypothesis that the electric neutrality of such catalysts is violated and consideration of anionic vacancies as participants in the catalytic process are not required to describe the thiophene hydrogenolysis mechanism on bimetallic sulfide catalysts. The low activation energy, *i.e.*, high degree of compensation of the energy consumed for the cleavage of 'old' valence bonds in the thiophene molecule, results from the redistribution of the excess energy which is evolved upon the adsorption of thiophene and hydrogenation of its ring inside the macromolecule of the active component. The high rate of the catalytic process (synergism) is ensured by the fast transfer of electrons and protons along the closed system of valence bonds in a macromolecule of the active component with an optimum chemical composition.

Synergism is found in the catalytic systems Cr–WS_2 and Ni–NbS_2, whereas pronounced antagonism is found in the systems V–WS_2, Mn–WS_2, Cu–WS_2, Zn–WS_2 and Ni–ReS_2 (see Ref. 135). In order to explain this effect within the framework of the method of interacting bonds, the heats of thiophene adsorption on bimetallic sulfide catalysts with different compositions were calculated.[136] Good correlation between the heat of thiophene adsorption and the catalytic activity of bimetallic sulfides was observed (Fig. 13). The non-additive decrease in the activity may be due to the formation of either very strong (Ti, V, Mn, Zn) or very weak (Cu) M—S bonds. In the framework of the concerted mechanism considered here, this can mean (provided that the source of activated hydrogen is the same and the metal ion of the first transition row has the same environment) that high strength of M—S bonds prevents the displacement of H_2S adsorbed on an active site by thiophene, whereas the weakness of the M—S bond does not allow thiophene to remain on the active site for a period of time sufficient for completing the catalytic cycle. Certainly, the electronic factor should now be considered for understanding the deeper reasons for this phenomenon. In order to reveal the nature of the thiophene–metal bonding, it is necessary to study the electronic structure of the transition metal ion in the active component using quantum-chemical methods and taking into account the possibility of hydrogen occlusion into the matrix; revealing the deep reasons for synergism (or antagonism) requires that 'cooperative' electronic properties of the active component with a given chemical composition be established.

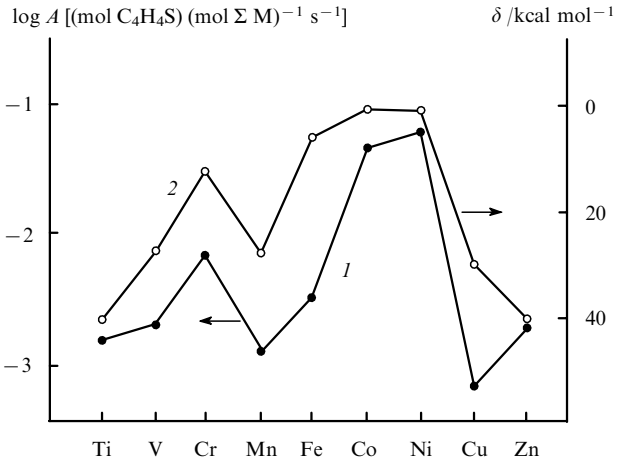


Figure 13. Dependences of activity (A) of catalysts in the hydrogenolysis of thiophene (curve *1*) and deviations of the enthalpy of thiophene adsorption δ (assuming the heats of adsorption on nickel and cobalt as the optimum values) on the nature of the metal contained in the active component of bimetallic sulfide catalysts (curve *2*).[136]

It was noted at the beginning of this section that concerted mechanisms are mainly known for acid–base reactions. In fact, it is hard to expect that the concerted mechanism would be realised in redox catalytic reactions where the catalyst surface undergoes successive reductions–reoxidations on exposure to the reaction medium as is the case in, *e.g.*, the 'classical' version of the hydrogenolysis mechanism of the C—S bond, according to which the MoS_2 surface first undergoes reduction to give an anionic vacancy and then undergoes reoxidation by a thiophene molecule (see the next section).

The concerted mechanism of thiophene hydrogenolysis considered here cannot be attributed to redox reactions, as it does not explicitly assume reduction and reoxidation of the sulfide catalyst surface. It should formally be considered as an acid–base mechanism. In fact, Ni(IV) or Co(III) ions in the d^6 electronic configuration located at the edge plane of the MoS_2 matrix are Lewis acid sites; the unshared electron pair of the adsorbing molecule (a base, *e.g.*, thiophene) is transferred to the vacant d_{z^2} and d_{xy} molecular orbitals of these sites. On the other hand, the coordinatively unsaturated sulfur atoms located at the $(01\bar{1}0)$ plane of the active component have an uncompensated valence bond and, as shown above, obtain an additional negative charge in the catalytic process. In other words, they act as a Lewis basic site that transfers electron density to the antibonding orbital of the hydrogen molecule which is being adsorbed, resulting in its dissociation. Thus, the electrically neutral macromolecule of the active component contains acid–base pairs; this is a prerequisite of the concerted mechanism. The electron density redistribution and the transfer of activated hydrogen to the thiophene molecule during the catalysis are not accompanied by changes in the formal oxidation states of the metals contained in the active component.

The concerted hydrogenolysis mechanism of the C—S bond on bimetallic sulfide catalysts, which has been proposed as an alternative to the generally accepted redox mechanism of this reaction, agrees completely with the concept of the common nature of heterogeneous, homogeneous and enzyme catalysis. The active component of sulfide catalysts is considered as an electrically neutral macromolecule containing acid–base pairs which serve as adsorption and activation sites for the reacting molecules. The high rate and selectivity of the catalytic process and the low activation energy are ensured by the synchronous activation of reacting molecules in the coordination sphere of the active component due to the fast transfer of electrons and protons along the closed system of valence bonds. This also ensures a high degree of compensation of the energy which has been spent for the cleavage of old bonds by the energy liberated in the exothermic steps of adsorption, hydrogenation and formation of new bonds.

IV. The concept of the determining role of the metal—sulfur bond energy in heterogeneous catalysis by metal sulfides

In the middle of the 1950s, G K Boreskov proposed a hypothesis about the determining role of the bond energy of oxygen with the surface of oxide catalysts in oxidation reactions.[137] This concept was developed most consistently in the studies by V V Popovskii (see Ref. 138 and references cited therein). However, it was found already at that time that, in many cases, partial oxidation and deep oxidation obey different rules. Therefore, a concept appeared simultaneously about a conjoint mechanism of interaction of reactants with each other and with the solid catalyst.[70]

Probably, the hypothesis on the participation of anionic vacancies of sulfide catalysts in the catalytic reaction was first put forward by Lipsch and Schuit,[139] although they did not give any experimental evidence for this mechanism.† Anionic vacancies

† It is this publication that was subsequently referred to most often to substantiate the role of anionic vacancies.

are formed on the surfaces of sulfide catalysts due to the reaction of the surface sulfur atoms with hydrogen at elevated temperatures, followed by removal of the sulfur atoms as hydrogen sulfide.

The following studies have been carried out in order to substantiate the concept of the determining role of the energy of bonding of sulfur atoms to surfaces of sulfide catalysts in their catalytic activity:

(1) estimation of the strength of bonding of sulfur to sulfide catalyst surfaces under conditions of their temperature-programmed reduction in hydrogen;

(2) determination of the mobility of surface sulfur atoms by measuring the isotope exchange rate between hydrogen sulfide from the gas phase and solid catalyst surfaces;

(3) quantum-chemical calculations of the electronic structure of the active site.

1. The strength of bonding of sulfur to sulfide catalyst surfaces

The temperature-programmed heating of solid catalysts in different gases (or gas mixtures) is a relatively popular and informative method for the study of the nature of surface compounds and possible intermediates of catalytic reactions.[140] Correlations between the strength of bonding of surface sulfur atoms to the catalyst, on the one hand, and its catalytic activity, on the other hand, for sulfide catalysts are most commonly determined using temperature-programmed reduction (TPR) in hydrogen. Hydrogen reacts with surface sulfur atoms to remove them as hydrogen sulfide and to form anionic vacancies:

$$M-S + H_2 \longrightarrow M-\square + H_2S,$$

where $\square$ is an anionic vacancy. It is assumed *a priori* that the amount of removed hydrogen sulfide can serve as a quantitative measure of the number of vacancies formed on sulfide catalyst surfaces.

It has been shown in one of the first studies [141] on the TPR of sulfide catalysts that the first maximum of the evolution of hydrogen sulfide from Ni–Mo and Co–Mo catalysts corresponds to 320 and 380 °C, respectively. A subsequent increase in the temperature is accompanied by the continuous evolution of H_2S. The continuous evolution of hydrogen sulfide from both mono- and bimetallic sulfide catalysts at temperatures above 300 °C found by Burch and Collins [142] was used as the basis for drawing the conclusion that nickel does not affect the nature of surface sulfur compounds.

On the other hand, the temperature-programmed reduction of bulk molybdenum disulfide starts at higher temperatures, *viz*., above 700 °C.[143] Non-stoichiometric sulfur (S_x) is found in catalysts supported on Al_2O_3; it can be adsorbed both on mono- and bimetallic sulfide catalyst surfaces. An analogy with the adsorption of oxygen on oxide catalysts is evident here. It is this non-stoichiometric sulfur that is readily hydrogenated with hydrogen at low temperatures, whereas the reduction of stoichiometric sulfides starts only at temperatures >500 °C, which is much higher than typical temperatures of catalytic reactions. Similar results were obtained in a study of sulfide Ni–W catalysts.[144] A mechanism of the formation of non-stoichiometric sulfur was proposed by Mangnus *et al*.[145]

No considerable difference between the TPR spectra of sulfide Co–Mo catalysts at low and high hydrogen pressures (1 and 31 atm, respectively) was found.[146] In both cases, low-temperature evolution of hydrogen sulfide was observed, which ceased at 200 °C. A further increase in temperature resulted in the evolution of an insignificant amount of H_2S; this amount increased at temperatures above 500 °C. Labruyere *et al*.[146] do not reject the possible formation of non-stoichiometric sulfur on catalyst surfaces due to the decomposition of hydrogen sulfide during their sulfidation; however, they do not rule out that other H_2S sources, *e.g*., SH groups, can exist.

We will not analyse other works that deal with the TPR of sulfide catalysts, since poorly characterised samples and samples thermally treated under non-comparable conditions were studied in most of them. The corresponding references can be found in the monograph by Topsøe *et al*.[4] and in studies cited above. Let us note just one short communication [147] describing an attempt to obtain direct experimental correlations between the M–S bond strength and the number of anionic vacancies, on the one hand, and the catalytic activity, on the other hand. However, the lack of sufficient information about the experimental conditions does not allow us to be sure that the conclusions are reliable.

2. The mobility of surface sulfur

Isotope exchange between molecular oxygen and oxygen in the solid oxide lattice (heteroexchange) was widely used for determining the mobility of surface oxygen in oxide catalysts.[70, 137, 138] Sulfide catalysts were also studied using the heteroexchange between ^{35}S-labelled hydrogen sulfide and the sulfur atoms in MS_2 crystal lattices. Lukens *et al*.[148] were probably the first to show that the heteroexchange between $H_2{}^{35}S$ and the surfaces of bulk or supported WS_2 occurs in toluene even at room temperature. These data were used to determine the specific surfaces of sulfide catalysts. In the gas phase, exchange occurs at 70 °C.[149]

Radioactive hydrogen sulfide was detected [150, 151] in thiophene hydrogenolysis products on sulfide catalysts containing radioactive sulfur. Analysis of pulse-mode kinetic curves allowed the conclusions to be drawn that catalyst sulfur atoms are involved in the reaction and that two types of sulfur atoms exist, *viz*., those capable of fast and slow exchange.

Systematic studies on the conversion of radioactive dibenzothiophene ([^{35}S]DBT) on different catalysts [152–154] made it possible to substantiate the hydrogenolysis mechanism of the C–S bond with involvement of anionic vacancies. The conclusions drawn were based on data on the appearance or disappearance of radioactive hydrogen sulfide in the hydrogenolysis products of [^{35}S]DBT upon periodic changes in the process conditions.

A study of the heteroexchange between $H_2{}^{35}S$ and surfaces of sulfide catalysts at high hydrogen pressures (10–50 atm) showed [155, 156] that the amount of 'mobile' sulfur does not depend on pressure but does depend on temperature. The ratio of the amount of 'mobile' sulfur to its total amount varied from 10% at 200 °C to 44% at 400 °C. A decrease in the hydrogen sulfide concentration in the gas phase decreased the exchange rate, but the amount of 'mobile' sulfur remained unchanged. It should be

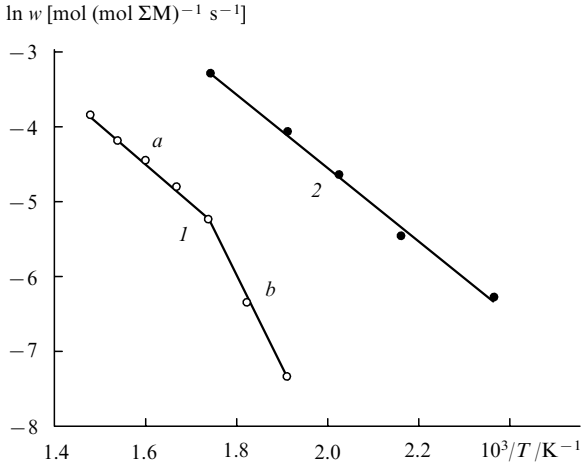


Figure 14. Temperature dependences of the rates of thiophene hydrogenolysis (*1*) and isotope heteroexchange of $H_2{}^{35}S$ (*2*) on sulfide Ni–Mo catalysts.[157]

The hydrogenolysis activation energy within segment *a* is 14 kcal mol^{-1} and that within segment *b* is 28 kcal mol^{-1}; the activation energy of heteroexchange is 10 kcal mol^{-1}.

stressed that exchange occurs with a measurable rate even at 200 °C, where the hydrogenolysis of the C–S bond is certainly impossible.

The heteroexchange of $H_2{}^{35}S$ in highly dispersed sulfide catalysts of 'organometallic origin' occurs at temperatures $\leqslant$150 °C.[157] A comparison of the temperature dependences of heteroexchange and hydrogenolysis of thiophene (Fig. 14) shows that at moderate temperatures (250–300 °C), the heteroexchange rate is 2–5 orders of magnitude higher than that of the catalytic reaction. At lower temperatures, the hydrogenolysis of thiophene that requires high activation energy does not occur at all, whereas heteroexchange, which is characterised by low activation energy, occurs readily. It was concluded on this basis[35,157] that the heteroexchange and hydrogenolysis on sulfide catalysts under conditions of the catalytic reaction occur simultaneously and independently following different unrelated mechanisms.

3. Quantum-chemical calculations

The hypothesis about the decisive role of the energy of bonding of sulfur to the catalyst surface dominates in the concept of the hydrogenolysis mechanism of the C–S bond on sulfide catalysts. Numerous attempts were made to substantiate this hypothesis from the standpoint that vacancies can be formed and involved in the coordination of sulfur-containing molecules, and also to explain the origin of the synergism discovered.

Duben[158] was probably the first to consider the electronic interaction of a thiophene molecule with a molybdenum ion. Although the active site model used (molybdenum in an oxygen environment) was inadequate, the expanded Hückel method made it possible to demonstrate the possibility of donor–acceptor interaction of a thiophene molecule and the vacant d_{z^2} orbital of a Mo^{4+} ion in the d^2 electronic configuration. Based on an estimate of the Mo–S bond strength, it was concluded that the Mo^{3+} active site in the d^3 electronic configuration is the most preferable for adsorption, as it ensures an energetically favourable possibility for the elimination of sulfur and regeneration of the active site.

A study of thiophene adsorption on a molybdenum cluster and on cobalt atoms in a hypothetical active site within the framework of the same expanded Hückel method showed,[159,160] albeit indirectly, that two ways of thiophene adsorption are possible, *viz*., either single-point adsorption on an anionic vacancy, or two- or four-point adsorption on cobalt atoms.

However, no studies on the electronic configuration of an active metal atom and its interaction with the substrate were carried out subsequently; instead, research mainly focused on the search for general regularities of catalytic properties as a function of the electronic structure of transition metal sulfides. It was found[161] that the reactivities of sulfides of metals belonging to the second and third transition rows in the dibenzothiophene hydrogenolysis differed by 2–3 orders of magnitude. On the other hand, this difference is small for metals of the first transition row. The attraction of this kind of studies was that the regularities obtained could provide a universal key for unravelling the catalysis by metal sulfides as a general phenomenon, since similar dependences of activity on the nature of the catalyst have also been found for other systems, including metals and oxides.[162] Binary transition metal sulfides have been well studied by physical and structural methods (see, *e.g*., Refs 163 and 164 and references cited therein). The covalency of the metal–sulfur bond, which makes the dominant contribution to the electronic structure of the disulfide, is an important property of binary sulfides used as the basis in theoretical studies.[165,166]

Calculations aimed at the determination of how the electronic structure of a transition metal depends on its position in the Periodic system and which electronic factor determines the catalytic activity have been performed in a series of studies.[166–168] The energy levels and charge distribution in octahedral clusters MS_6^{n-} were analysed in a calculation by the scattered wave method (SCF-Xα). Metals of the first and second transition rows were used as central atoms in these clusters; the formal oxidation state of sulfur was taken to be 2–, whereas the formal oxidation state of the metal corresponded to that found experimentally. It was found that the calculated covalency of the M–S bond did not correlate explicitly with the sulfide activity. On the other hand, a correlation was found between the number of d-electrons in the HOMO of the transition metal and the activity of its sulfide. Based on the analysis of the HOMO symmetry, it was concluded that not only the presence of a certain number of electrons in the HOMO but also its $2t_{2g}$-symmetry are prerequisites for high activity. In view of this, a new parameter B was introduced, which specifies the strength of the given bond:

$$B = n_\sigma D_\sigma + n_\pi D_\pi ,$$

where the D_σ and D_π values determine the contribution of the metal d orbitals to the σ- and π-bonding orbitals of the molecule, whereas n_σ and n_π are the numbers of the σ- and π-bonding electrons, respectively. Thus the products $n_\sigma D_\sigma$ and $n_\pi D_\pi$ are measures of the relative contributions of the σ- and π-components to the M–S bond strength. However, the correlation still remained unsatisfactory; therefore, yet another parameter was introduced, *viz*., the bond activity parameter A_2:

$$A_2 = nB,$$

where n is the total number of electrons.

Although this resulted in a relatively good correlation between A_2 and catalytic activity,[166] the physical meaning of this parameter is vague.

This approach was used to explain the nature of synergism in bimetallic sulfide catalysts of hydrotreating. The $[M'MoS_9]^{n-}$ cluster, where M′ is a metal of the first transition row, was used as the model. This cluster consists of two MoS_6 octahedra sharing three sulfur atoms at their base. The calculations show[166,167] that if M′ = Co or Ni, the electrons from the $3d(e_g)$ orbital of the 'promoter' atom are transferred to a lower orbital of molybdenum, *viz*., $4d(t_{2g})$, resulting in the formal reduction of molybdenum. If M′ = Cu, the electron transfer occurs in the reverse direction. No electron transfer occurs in the case of Fe and Zn; for other metals of the first transition row, the situation is uncertain. Thus, the promoting effect is explained by the electron transfer from a promoter's orbital to the antibonding orbital of molybdenum. Since these electrons are located on an antibonding orbital, the Mo–S bond strength decreases, which results in a decrease in parameter B and an increase in the catalytic activity. Thus, the role of a promoter is to increase or decrease the number of electrons on the antibonding orbital of molybdenum: the higher the electron density on the metal the higher the catalyst activity. Anionic vacancies play the role of active sites; their formation is facilitated when the Mo–S bond weakens.

However, the correlations found do not explain why a linear combination of calculated electronic parameters determines the catalytic properties of binary sulfides of transition metals. Therefore, Topsøe *et al*.[4,169,170] carried out *ab initio* calculations of the energy-band structures of these catalysts. All calculations were based on the idea of the determining role of the M–S bond strength in the catalyst activity; therefore, the hypothesis was called the bond energy model (BEM). This model considers the hybridisation of the valence states of sulfur with the d-states of the transition metal and hybridisation of the states of sulfur with the s-states of the metal. Different terms were combined to calculate the total bond energy of sulfur in binary sulfides of transition metals. The M–S bond strength was in good correlation with the observed catalyst activity; it was therefore concluded that the activity of transition metal sulfides originates from the difference between the energy gain due to the hybridisation of the metal states with sulfur valence states and the energy loss due to the weakening of the metal–metal bond when sulfur atoms are located on the surface. This viewpoint differs fundamentally from that considered above as, according to it, the maximum catalyst activity is reached at some optimum M–S bond strength.

Thus, the hydrogenolysis rate of the C–S bond should be proportional to the concentration of anionic vacancies on the surface of sulfide catalysts, which depends on the composition of the reaction mixture and the M–S bond strength.

At the next stage of the BEM development, the possibility of the formation of vacancies on an edge plane of a single molybdenum disulfide slab was considered.[171] It was shown within the framework of the density functional theory (DFT) that the elimination of a sulfur atom from the $(30\bar{3}0)$ MoS_2 edge plane (see Fig. 10) requires no less than 326 kJ mol^{-1}. Considerably less energy (46 kJ mol^{-1}) is required to eliminate sulfur from the $(10\bar{1}0)$ edge. It is noteworthy that the interatomic distances in a single molybdenum disulfide slab without anionic vacancies, calculated within the DFT method, differ noticeably from the corresponding distances in a single crystal. Byskov *et al.*[171] explain this by the fact that only a relatively small part of the surface was considered in the calculations.

If part of the molybdenum atoms is replaced by cobalt atoms, the elimination of a sulfur atom bonded both to molybdenum and cobalt becomes thermodynamically favourable and gives an energy gain of 34 kJ mol^{-1}. On the other hand, the 'remaining' sulfur atom is very strongly bound to the matrix (222 kJ mol^{-1}). This fact agrees with the calculated Co–S bond lengths (2.34 Å in the former case and 2.24 Å in the latter).

Byskov *et al.*[172] undertook an attempt to determine the geometric form of an active component with the maximum possible number of anionic vacancies, which they believe to be necessary to acquire the maximum catalyst activity. Since the possible number of anionic vacancies at the edge plane of a regular hexagon is quite limited (see Fig. 10), it was assumed that the geometric shape of the active component can be a dynamic function of the reaction conditions. It was found that the maximum concentration of active sites (anionic vacancies) per unit volume is provided by the triangular configuration of the active component. DFT calculations confirmed that the higher the structure defectiveness of the active component the lower the M–S bond strength and the higher the catalyst activity.

The study by Byskov *et al.*[171] was based on studies of molybdenum sulfide nanoclusters by scanning tunnelling electron microscopy (STM).[173, 174] The nanoclusters were obtained by sputtering molybdenum atoms on the surface of an Au(111) single crystal in hydrogen sulfide at 127 °C followed by annealing at 400 °C (also in hydrogen sulfide). It was shown by STM that the sample contained islets, mainly triangular, with a mean side length of 30 Å; these are molybdenum sulfide nanoclusters whose basal plane (0001) is oriented parallel to the Au(111) plane. Analysis of nanocluster images obtained at atomic resolution made it possible to establish that the interatomic distances in it are 3.15 ± 0.05 Å, *i.e.*, they are the same as those in molybdenum disulfide. This served as the basis for the conclusion that this method gave a triangular MoS_2 nanocluster, whose edge planes are limited by single sulfur atoms located in irregular lattice positions. After treatment of the cluster with atomic hydrogen, pictures obtained at atomic resolution revealed point defects, *i.e.*, anionic vacancies. The authors claim that they were the first to observe the active site of a catalytic reaction.

Without doubt, these studies [173, 174] have been carried out on the highest experimental level and can be regarded as classical studies of solid surfaces. The results obtained in these studies had a certain resonance in scientific circles (see, *e.g.*, Ref. 175). However, let us try to consider the results described above from the viewpoint of the consistency of the picture obtained with real catalytic systems.

First, the unusual triangular shape of the species is doubtful: the most thermodynamically stable shape of any isolated system is a sphere [176] (or a circle for two-dimensional systems). It was confirmed experimentally that a regular hexagon is the most thermodynamically stable shape of a single molybdenum disulfide slab. The triangular shape of the species indicates that molybdenum disulfide nanoclusters possess an excess of internal energy. The invariability of this shape after annealing at 400 °C in a hydrogen sulfide atmosphere is only possible in the case of strong epitaxial interaction of the nanocluster with the surface.

In fact, the Au(111) plane is a hexagonal closely packed structure with the Au–Au distance of 2.884 Å. It is well known [177] that epitaxial interaction of solids is only possible if the symmetry groups of the interacting bodies are the same and the interatomic distances are equal to within 10%. In this case, such a coincidence is in fact observed: molybdenum disulfide has a hexagonal densely packed structure with a lattice parameter of 3.16 Å, which differs from the lattice parameter of gold by less than 9%. If the symmetry of the crystal lattice differs from that of the nanocluster, single slabs of molybdenum disulfide are oriented orthogonally to the substrate surface on which they have been deposited by some method (see Ref. 111). This is explained by the absence of strong chemical interaction between the basal surface of molybdenum disulfide and the substrate surface. Therefore, stabilisation occurs due to the formation of chemical bonds between the atoms of the MoS_2 edge plane and the support atoms. For example, parallel orientation of slabs was observed in the MoS_2/Mo(111) system.[178]

The second important criticism also corresponds to the shape of the nanocluster species. It is easy to show (see, *e.g.*, Ref. 179) that MoS_2 species of any shape that differs from the regular hexagon are non-stoichiometric; as a result, the macromolecule is no longer electrically neutral. If the species are triangular, sulfur atoms are present in a considerable excess, which inevitably results in a charged cluster $[MoS_x]^{n-}$. Since epitaxial growth implies the electronic interaction of the substrate with the support, one should expect the electron density transfer from the surface atoms of the support to the triangular nanoclusters of MoS_2. Thus, a considerable excess of sulfur atoms is inconsistent with the conclusion drawn by the same authors [173, 174] regarding the 'inherent' defects of the molybdenum disulfide structure.

The third important issue is related to the discovery of defects (anionic vacancies) after treatment of a nanocluster with atomic hydrogen. As the authors state,[173, 174] a side of the triangle consists of sulfur atoms located in irregular positions of the nanocluster crystal lattice. It is these sulfur atoms that are eliminated upon the reaction of a cluster with atomic hydrogen. On the other hand, according to their calculations,[171] elimination of these atoms requires an energy of 326 kJ mol^{-1}. This means that elimination of these atoms is impossible under catalysis conditions, and this defect can exist only in ultra-high vacuum.

Finally, there is the fourth important issue. The model suggested by Byskov *et al.*[171] assumes the existence of 'inherent' defects, *viz.*, anionic vacancies.‡ It is known (see, *e.g.*, Ref. 180) that the linear size of the active component in the most active catalysts is no higher than 10–15 Å. An electrically neutral $(MoS_2)_x$ macromolecule of this size is shown in Fig. 10. On an alumina surface, the active component can have the form of filiform structures up to 50 Å long and several atomic layers high. This is the type of structure considered within the BEM approach. The number of 'inherent' defects in such a structure should be one per cobalt atom or one per two molybdenum atoms. It is easy to see that in this case a single filiform MoS_2 slab should be represented as Mo_2S_3, as the number of anionic vacancies should match the number of defects. Table 7 lists the interatomic distances in a Mo_2S_3 single crystal published by Jonge *et al.*[181] and the interatomic distances calculated for a defective molybdenum disulfide structure.[171] One can see that these interatomic distances agree well, which is not surprising: the elimination of a sulfur atom

‡ It should be noted that a strong deformation of the MoS_2 slab structure results in new interatomic distances, which favours weakening of the Mo–S bonds. The introduction of cobalt deforms the structure of a MoS_2 slab further. In the most active catalysts, the defectiveness reaches a maximum value, so that a vacancy appears at each cobalt atom.[172]

Table 7. Interatomic distances in the structure of a Mo_2S_3 single crystal and in the defective structure of molybdenum disulfide.

Bond	Interatomic distances (Å) in	
	single crystal Mo_2S_3 [181]	defective structure [171]
Mo – Mo	2.86	2.85
	3.208	3.12
	3.22	–
Mo – S	2.31 – 2.72	2.34 – 2.43

from the MoS_2 structure must inevitably be accompanied by the reduction of Mo(IV) into Mo(III). However, reduced forms of molybdenum disulfide have not been found in any XPS studies of sulfide catalysts. Furthermore, it was reported [181] that Mo_2S_3 is crystallised in monoclinic system with space group $P2_1/m$ (C_{2h}^2), which differs from the MoS_2 symmetry group (see Table 1). It is MoS_2 species that are always detected by high-resolution electron microscopy.

Thus, studies by Topsøe *et al.*[169–174] contain an internal logical contradiction between the experimental results and theoretical calculations, which they invariably interpret in favour of the bond energy model they are developing, without consideration of the laws of thermodynamics and structural chemistry.

The bond energy concept was also used as the basis of a series of studies carried out by Raybaud *et al.*[182–186] They used the *ab initio* DFT method to study the crystal structure and the electronic and energetic properties of over 30 transition metal sulfides.[182, 184] The calculations took into account the actual crystal structure of each sulfide and the possibility of rearrangement (relaxation) of surface atoms in comparison with bulk atoms. The cohesion energy, *i.e.*, intermolecular bonding, was calculated in these studies, unlike in other works.[169–174] As opposed to the standard heat of formation of sulfides, the cohesion energy is the atomisation energy of a compound. Thus, the energy of each particular bond is a fraction of the total intermolecular interaction energy. In the simplest case, the strength of the M – S bond can be determined as the intermolecular cohesion force divided by the number of valence bonds in a unit cell. The M – S bond strength calculated this way correlates very well with the activity of catalysts measured by Pecoraro and Chianelli.[161] However, it should be noted that the bond energies found reflect the actual strength of the M – S bond in the sulfide and are totally unsuitable for kinetic equations for a catalytic reaction. In fact, the M – S bond strength is 210 kJ mol^{-1} in the most reactive sulfide, *viz.*, RuS_2, and 251 and 272 kJ mol^{-1}, respectively, in the less reactive sulfides MoS_2 and WS_2. On the other hand, it is well known that the activation energy of the catalytic hydrogenolysis of the C – S bond is 42–63 kJ mol^{-1} (see, *e.g.*, Ref. 8). If we assume that the elimination of a sulfur atom from the active site is the limiting step, the bond energy of sulfur with this site should not exceed the activation energy.

The DFT method was used to calculate the geometric structure of the surface of a single MoS_2 slab and the electronic structure of molybdenum at the edge plane of this slab.[183] According to the data obtained, the $(30\bar{3}0)$ edge plane undergoes a noticeable rearrangement: the surface molybdenum atoms are shifted by 0.04 Å into the macromolecule, whereas the surface sulfur atoms are shifted by 0.6 Å in the opposite direction. In our opinion, this agrees very well with the structure of a real macromolecule affected by surface tension forces. Yet another important conclusion drawn by Raybaud *et al.*[183] is that a rearranged side of a macromolecule is stable at least up to 400 °C.

Finally, the localisation sites of cobalt in the MoS_2 structure were considered.[186] It was found that the replacement of molybdenum atoms by cobalt atoms inside a macromolecule and the coordination of cobalt to sulfur atoms at the $(10\bar{1}0)$ edge plane are less energetically favourable than the replacement of molybdenum atoms at the $(30\bar{3}0)$ edge plane of a single MoS_2 slab. The optimised interatomic distances Co – S and Co – Mo, which are 2.21 and 2.84 Å, respectively, are in good agreement with the values found experimentally using EXAFS. Based on the concept of the determining role of the M – S bond strength in the catalyst activity, the enthalpy of adsorption of sulfur atoms on metal atoms at the edge plane of a MoS_2 slab was calculated. It should be emphasised that it was the adsorption on coordinatively unsaturated metal atoms that was considered, not the formation of anionic vacancies which was postulated in the previous works. It is believed that the adsorption of sulfur (probably H_2S, as indirectly follows from Ref. 186) involves two adjacent metal atoms simultaneously. The adsorption of sulfur on two cobalt atoms is a weakly isothermic process (the heat of adsorption is 3.8 kJ mol^{-1}). The heat of adsorption of sulfur on the Co – Mo pair increases to 9.6 – 28.9 kJ mol^{-1} and reaches a maximum value on the Mo – Mo pair (122 kJ mol^{-1}). On the other hand, the adsorption of sulfur on the Ni – Ni and Cu – Cu pairs is endothermic (– 38 and – 113 kJ mol^{-1}, respectively). The heats of adsorption of sulfur on single metal atoms were not reported in this work, which, as we believe, may be due to their negative values. We calculated the heats of adsorption of sulfur-containing molecules and found [84] that Ni(II) and Co(II) ions cannot adsorb donor molecules. Such adsorption becomes possible only if these atoms are bound to occluded hydrogen and the active metal is in the d^6 state.

We are not going to analyse other theoretical studies in detail as this would require a separate review on this subject. Let us just note some remarkable results directly related to the subject of our paper. For example, it was shown [187] that no less than 5 eV is required to create an anionic vacancy in an end face of a molybdenum disulfide molecule. Smit and Johnson,[188] who considered the bond strength of the 3p orbitals of sulfur with the d orbitals of metals, attributed the greatest importance to the metal oxidation state: as a result of the electron density transfer from nickel or cobalt atoms to molybdenum, their oxidation states became higher than those in the binary sulfides. A similar electron density transfer from the Ni atom to MoS_2 was observed by Collman *et al.*[122] They considered the adsorption of thiophene on coordinatively unsaturated atoms rather than on anionic vacancies (the adsorption of pyridine occurs similarly [189]). The totally optimised hexagonal structure of an electrically neutral cluster $Mo_{27}S_{54}$ was calculated.[190, 191] According to the calculations, the adsorption of thiophene occurs on the molybdenum atoms located in the vertices and edge planes of this cluster; anionic vacancies were not considered.

Thus, although many authors initially postulate that the M – S bond strength has a determining role in the activity of sulfide catalysts (*i.e.*, that anionic vacancies are involved in catalytic transformations), the majority of them eventually consider the interaction of sulfur-containing molecules with coordinatively unsaturated surface metal atoms. We believe that this is quite an objective reflection of the real situation that the active sites of heterogeneous catalysts participate in the catalytic process.

In conclusion, let us offer several additional arguments against the involvement of anionic vacancies in the catalytic cycle. A thermodynamic estimate of the possibility of formation of anionic vacancies in the MoS_2 and WS_2 structures by the interacting bonds method showed [192] that the appearance of such bonds in a hydrogen atmosphere is unfavourable since the adsorption of hydrogen sulfide on a vacancy gives a much larger energy gain. Therefore, the equilibrium

$$M-S + H_2 \rightleftharpoons M-\square + H_2S$$

is always shifted to the left under catalytic reaction conditions.

Direct experimental proof of the absence of correlation between the MoS_2 activity and the concentration of anionic vacancies was obtained in an *in situ* study of the electric conductivity of a MoS_2 single crystal under conditions of pulse-mode hydrogenolysis of butanethiol.[193–195] A MoS_2 single crystal reduced in a stream of H_2 at 257 °C contained over 10^{18} electrons

per cm^3, which corresponded to the concentration of anionic vacancies. After a portion of butanethiol was injected, the conductivity decreased abruptly and then increased without reaching its original value. The degree of butanethiol conversion did not exceed a few percent. Periodic injection of new portions of butanethiol decreased the conductivity (decreased the concentration of anionic vacancies) and increased the conversion. The conversion in the absence of n-type conductivity was ~100%. Thus, an increase in the concentration of anionic vacancies during the reduction of MoS_2 results in a decrease in its reactivity in the hydrogenolysis of the C–S bond, whereas, on the contrary, a decrease in their concentration due to the surface upbuilding by sulfur from the gas phase is accompanied by an increase in the catalytic activity.

Doping of a MoS_2 single crystal with Co^{2+} ions results in p-type conductivity;[193–195] the concentration of current carriers is almost independent of the thermal treatment conditions in an H_2 or He atmosphere and does not change during the catalytic reaction. The conversion of butanethiol under these conditions is close to 100%. On the one hand, it means that Co stabilises the MoS_2 structure and hinders its reduction. On the other hand, these data confirm again that the involvement of anionic vacancies in a catalytic reaction is not mandatory.

As noted above, sulfide catalysts are highly dispersed systems that operate steadily under real conditions at high temperatures (350–380 °C) and hydrogen pressures of 20–150 atm for long periods (months and years). The following calculations may be shown as an example. The hydrogenolysis rate of dibenzothiophene (the main contaminant in diesel fuel) at 400 °C is ~3 (g S) (g Co)$^{-1}$ h^{-1} (see, *e.g.*, Ref. 165). Let us assume that the liquid hourly space velocity of diesel fuel containing 0.5% sulfur is 5 g (g Cat)$^{-1}$ h^{-1} (where Cat stands for the catalyst). If the catalyst contains 3% of cobalt, it turns out that 0.8 (g S) (g Co)$^{-1}$ h^{-1} passes through it. Thus, at 100% conversion of dibenzothiophene and under the condition that each cobalt atom has an anionic vacancy and can accelerate the reaction, three-fourths of the vacancies are not involved in the catalytic cycle at each time instant but are necessarily present on the surfaces of highly dispersed species. Hence, the active component is a highly defective structure which, nevertheless, works in a stable mode for a period of one year; each active site undergoes a reduction–reoxidation cycle more than 50 000 times during this period.

On the contrary, we believe that the site centre of sulfide catalysts is a thermodynamically stable system[§] with a minimum amount of structural defects.

A brief analysis of studies that dealt with the bond energy model shows that there is a trend to reconsider its fundamental postulate, namely, it is admitted more and more often that it is a coordinatively unsaturated metal atom rather than a point defect in the active component crystal structure that serves as an active site. This concept is consistent with that of the concerted mechanism of action of sulfide catalysts which is being developed at the Institute of Catalysis. Indeed, many experimental facts interpreted within the bond energy model can be explained in terms of the synchronous interaction of reacting molecules in the coordination sphere of a bimetallic active site. For example, the M–S bond strength is identical to the heat of adsorption of a sulfur-containing molecule on the active metal atom. Thus, the necessity of an 'optimum bond strength' becomes clear.[136] The fast heteroexchange of ^{35}S at low temperature [148–157] should be considered as the intermolecular exchange of an adsorbed hydrogen sulfide molecule with the structure-building sulfur atoms of the active component. It is quite obvious that such exchange does not require a considerable consumption of energy. The temperature-programmed heating of a sulfide catalyst in hydrogen or in an inert gas atmosphere results in the elimination of adsorbed hydrogen. This follows decisively from a study of the benzene hydrogenation on sulfide catalysts under non-steady-state conditions.[196–198]

We hope that further progress in the study of the mechanism of action of sulfide catalysts will result in merging of the two alternative concepts into a unified theory of catalysis by metal sulfides.

V. Conclusion

Sulfide catalysts of hydrotreating of oil fractions constitute one of the best-studied and thoroughly characterised systems in heterogeneous catalysis. The success in the studies of these catalysts was considerably favoured by the specific structure of their active component, which is easily recognised among various supports and catalytically inactive surface compounds. However, we are still far from the understanding of the fundamentals of the nature of the catalytic action of sulfide catalysts. The generally accepted views that have been elaborated as a result of studies in areas bordering heterogeneous catalysis turned out to be unsuitable for describing many regularities of catalytic reactions on sulfide catalysts. However, the knowledge of the structure of the active component of these catalysts offers wide opportunities for the understanding of the fundamental bases of heterogeneous catalysis.

The concerted mechanism of action of sulfide catalysts described above is based on the principle of the common nature of heterogeneous, homogeneous and enzyme catalysis as a natural phenomenon. We believe that the active component of a solid catalyst is an electrically neutral macromolecule containing sites of adsorption and activation of substrate molecules. The chemical transformation of the substrate occurs in the coordination sphere of the active component without involvement of structure-forming atoms. Any point defects, including anionic vacancies, should be considered as a result of deviation of this system from the equilibrium state, which should have irreversible consequences, *viz.*, catalyst deactivation, poisoning of active sites, side processes, *etc.*

Below we formulate the main specific features of the concerted mechanism of thiophene hydrogenolysis on sulfide hydrodesulfurisation catalysts.

1. The chemical reaction occurs in the coordination sphere of the bimetallic sulfide active component without involvement of structure-forming atoms in the catalytic cycle.

2. The active sites of thiophene adsorption consist of Ni(IV) or Co(III) atoms in the d^6 electronic configuration. Adsorption occurs due to the interaction of the unshared electron pairs (n_σ and n_π) of sulfur atoms of a donor molecule with vacant d_{z^2} and d_{xy} orbitals of the active metal atom.

3. An indispensable part of the active site consists of an occluded hydrogen atom that appears in the active component due to oxidative addition of a hydrogen molecule to Ni(II) and Co(II) ions during the catalyst sulfidation. The occluded hydrogen is located in the matrix of a single MoS_2 slab in the centre of an 'empty' trigonal prism formed by sulfur atoms, under a nickel (cobalt) atom at a distance of 1.5 Å from it.

4. The activation of hydrogen occurs on paired 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 terminal sulfur atoms that border an electrically neutral macromolecule of the active component and act as the Lewis basic site. The excess 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

§ Molybdenite, a natural mineral consisting of MoS_2, is one such stable structure; furthermore, molybdenum disulfide is formed upon thermal decomposition of many molybdenum compounds with sulfur-containing ligands.[111]

bonds within an electrically neutral macromolecule of the active component.

6. The low hydrogenolysis activation energy is explained by the high degree of compensation of the energy required for the cleavage of 'old' bonds in a thiophene molecule by the energy liberated in exothermic processes of adsorption and hydrogenation of the thiophene ring.

7. The concerted mechanism of thiophene hydrogenolysis on sulfide hydrodesulfurisation catalysts corresponds to the class of acid–base heterogeneous catalytic reactions.

8. The concerted mechanism is also applicable to other sulfide catalysts that are crystallised 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 difficulties in finding such mechanisms are created by the non-uniform composition of the surface compounds and the possibility of their transformation on exposure to the reaction medium. This complicates considerably the analysis of kinetic regularities and makes it necessary to build complex kinetic models. Obviously, the solution to this problem should be searched for on the route to creating heterogeneous catalysts with homogeneous composition and with a known structure of the active component.

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