

Review

Concerted mechanisms in heterogeneous catalysis by sulfides[☆]

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Abstract

This paper summarizes some new evidence for the possibility of concerted mechanisms in the heterogeneous catalysis by sulfides. Several aspects are discussed: main regularities of thiophene and THT hydrogenolysis mediated by the well-characterized sulfide catalysts of different composition; electronic structure of the metals entering into the composition of the active component of both bulk and supported sulfide catalysts; mechanism of the active centers formation caused by the oxidative addition of dihydrogen to the active Ni (Co) metals and occlusion of hydrogen atoms into the MoS₂ matrix; mechanism of the homolytic hydrogen adsorption on the sulfide hydrotreating catalysts; synchronous interaction of the reactive molecules in the coordination sphere of the bimetallic active centers — proton and electron transfer; use of the energy released during exothermic reaction steps in the catalytic cycle. Catalytic transformations over the sulfide HDS catalysts are considered to belong to the acid–base catalysis. The profound identity of the mechanisms of heterogeneous, homogeneous and enzyme catalysis is discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. Concerted and stepwise mechanisms in the heterogeneous catalysis

At present, the key role in catalytic reactions is regarded to play an intermediate chemical interaction of reactive molecules with the definite active centers of catalysts. The intermediate interaction facilitates the chemical bond scission in the reactive molecules due to a high degree of energy compensation. This concept concerns with homogeneous, heterogeneous and enzyme catalysis and is intensively advancing at the Boreshkov Institute of Catalysis [1–4]. Studies on a molecular level made possible to understand a profound identity in the structure of the active sites and in the mechanisms of catalytic functioning of homogeneous, heterogeneous and enzyme catalysts. This is especially true for the acid–base catalysis [2,4].

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Bronsted and Lewis acid sites are known to play an important role in a number of catalytic reactions occurring in solutions and on the solid surfaces. As shown by Zamaraev and Zhidomirov [2], Zamaraev [4] and Kazansky et al. [5] in some cases, when acid and base centers are closely located and have an appropriate mutual orientation, possibilities for concerted mechanisms of acid–base catalysis may arise. The concerted mechanisms are widely spread in the enzyme acid–base catalysis. Zamaraev et al. [4,6,7] has recently demonstrated that concerted mechanisms take place for various acid–base transformations of organic molecules proceeding in the coordination sphere of metal complexes. As was shown, synchronous proton or hydrogen atom transfer through the chain of chemical and hydrogen bonds in cyclic intermediates can be important for quite a broad class of organic reactions proceeding in the coordination sphere of metal complexes. According to Zamaraev [4], the concerted mechanisms are most abundant in enzyme acid–base catalysis, where complex acid–base transformations occur in the presence of enzymes under mild conditions, at fast rates and very high selectivities; various acid–base transformations of organic molecules proceeding in the coordination sphere of metal complexes via the synchronous transfer of a proton or a hydrogen atom through the chain of chemical and hydrogen bonds in the cyclic intermediates. This mechanism may also occur in the heterogeneous catalysis as well, if there is a definite geometric agreement between the structure of a substrate and the active center.

In heterogeneous catalysis, the elucidation of the nature and mechanisms of intermediate chemical interaction of reactive molecules with the surface of solid catalysts is especially complicated by the following factors:

- Non-uniform composition of the catalyst surface, when the surface of solids can be represented with two or more surface species different in chemical composition and structure; in this case one may expect a number of catalytic reactions yielding different reaction products in the gas phase;
- Chemical transformation occurs at the phase boundary, therefore the surface coverage with adsorbed molecules can vary in a wide range depending on the reaction conditions;
- Structure of active sites is unknown in most cases;
- Up to now there are no sensitive physical methods (like multinuclear NMR spectroscopy in homogeneous catalysis) to investigate in situ of adsorption and transformation of the reactive molecules on the surface of *real* catalysts under the *real* catalytic conditions;
- Heterogeneous catalytic reactions occur, as a rule, under severe conditions (high temperature and (or) pressure), when the phase and structure transformations of the active component are possible.

Thus, a solid catalyst with an unknown structure of the active sites can be represented as a “black box” (Fig. 1): the total chemical composition of all catalysts is known, using some modern physical, chemical and kinetics methods one can obtain some responses to external action and one can formulate some regularities of the given catalytic reaction. This is especially true for oxide catalysts of complete and partial oxidation.

For years, the fundamental studies of the detailed mechanism and reaction kinetics were carrying out using different types of oxide and metal catalysts in relation with partial and complete oxidation of different substrates. These researches were initiated by G.K. Boreskov, the founder and first director of the Institute of Catalysis. G.K. Boreskov has made a key contribution to the theory of oxidative catalysis. In particular, he advanced the concept that the rate of complete oxidation reactions is determined by strength of oxygen binding to the oxide surface. In numerous investigations, Popovsky and coworkers (see, e.g., Ref. [8]) have demonstrated that the rate of complete oxidation of different substrates (hydrogen, methane, benzene, CO, etc.) over bulk binary and complex oxides

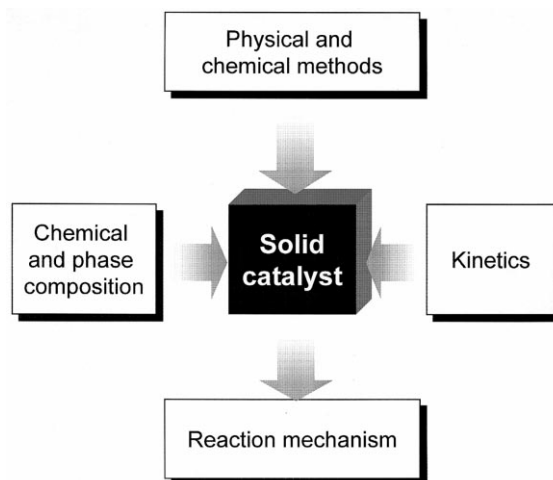


Fig. 1. Investigation of the mechanism of heterogeneous catalytic reactions mediated by the solid catalyst with an unknown structure of the active component.

correlates with the strength of oxygen binding and the rate of hetero-molecular exchange of oxygen with the catalyst surfaces. Ven'yaminov et al. (see, e.g., Ref. [9]) have substantiated the possibility of the redox stepwise mechanisms of various molecules oxidation. In this manner the concept of the binding energy in the heterogeneous catalysis by oxides has appeared.

Nevertheless, Boreskov [3,10] have demonstrated that concerted (or associative, or synchronous) mechanisms are also possible for oxidative reactions over oxide catalysts. In particular, hydrogen oxidation over both bulk and silica supported MoO_3 catalysts, prepared by impregnation (Table 1, [11,12]), occurs at a temperature as high as 400°C . Under similar reaction conditions the rate of catalyst reduction is slightly slower, and the rate of hetero-exchange of molecular oxygen is two orders of magnitude lower. But when the oxide catalysts were prepared via anchoring the Mo alkoxide complexes to the silica surface, the activity was observed at 100°C and no hetero-exchange occurs up to 250°C . This means, that the surface oxygen cannot be involved into the catalytic cycle. Hence, concerted mechanisms can be also observed in the heterogeneous catalysis by oxide as well.

Thus, the concerted mechanisms are possible for both biological and non biological homogeneous and heterogeneous catalysis. This phenomenon is caused by certain favorable for catalysis position of fragments of active sites and reactant molecules. The concerted mechanisms in catalysis are characterized with high rate of chemical transformations, low activation energy due to a high degree of the energy compensation, very high selectivity towards reaction products. During the catalysis,

Table 1

Comparison of the rates of catalytic transformation and the mobility of the surface oxygen atoms in the silica-supported oxide catalysts

Catalyst	T ($^\circ\text{C}$)	Rate (molecule/Mo. s) of		
		H_2 oxidation	Reduction	Hetero-exchange
$\text{MoO}_3/\text{SiO}_2$ (impregnated)	250	0	0	0
	450	2×10^{-4}	1×10^{-4}	4×10^{-6}
$(\geq \text{Si-O})_2\text{MoO}_2$ (MCO) ^a	250	8×10^{-3}	1×10^{-4}	0
	450	16×10^{-3}	5×10^{-4}	6×10^{-7}

^aMetal complex origin; the catalysts were prepared via anchoring of the Mo alkoxide complexes to the silica surface.

several molecules of reactants can be involved into the catalytic cycle, but no reaction intermediates, desorbed from the active site, are observed. The concerted mechanism is taken to occur via the synchronous interaction of the reactive molecules in the coordination sphere of the multifunctional active component resulted from the intermediate chemical interaction with a catalyst. The active component is likely to be either a single atom, or an assembly of atoms, or a metal complex, or an electroneutral macromolecule of a definite composition and structure.

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

The advancement in catalysis by sulfides seems to be based on the concepts of catalysis by oxides, because at that time (in the early 1970s) the catalysis by oxides was rather well studied. But sulfide catalysts possess an unquestionable advantages over oxide catalysts, because the nearest surrounding of active metals composes of sulfur atoms, therefore, sulfide species can be readily observed over the surface of both oxide and carbon supports. Besides, all sulfides are characterized with a more regular structure of the crystal lattices. Appearance at the same time of new and powerful techniques to investigate the solid catalyst surfaces seems to be the second factor, which pre-determined success in the recognizing structure of the active component of the sulfide HDS catalysts. Evidently, one may believe, that now it is generally accepted the active component of the sulfide HDS catalysts to be crystallized in the molybdenite structural type with Ni (or Co) atoms being located at the edge plane of a single slab of MoS_2 (or WS_2). However, even if similarity of the active component and MoS_2 structure does not cause any doubt, there is not consensus regarding the Ni (Co) localization. At least two possible versions were considered:

- Square–planar surrounding of Ni (Co) atoms with 4 S atoms at the edge plane of a MoS_2 (WS_2) single slab; in this case very short distances $\text{Ni–S} = 2.2 \text{ \AA}$ and $\text{Ni–W(Mo)} = 2.4 \text{ \AA}$ are observed [13,14]. These short Ni–S distances are characteristic of square–planar complexes with S-containing chelate ligands.
- Square–pyramidal surrounding of Ni (Co) atoms with 5 S atoms [15–19]. Elongation of the Ni (Co)–Mo distances up to 2.8 \AA results probably from the adsorption of a donor molecule, H_2S in particular.

But in our opinion, there are no contradictions between the versions. As was demonstrated in [20,21], Ni atoms in the square–planar surrounding with S atoms have a d^8 -electronic configuration and cannot adsorb donor molecules. The square–planar surrounding of Ni in the sulfide HDS catalysts, found in our study with EXAFS [14], results probably from the specific conditions of the sample preparation for EXAFS studies: after sulfurization at 400°C the patterns were evacuated at this temperature, therefore the adsorbed H_2S and the occluded hydrogen can be removed from the catalysts. Later, this suggestion was confirmed on EXAFS studies of other catalytic systems [22]. Hence, now we believe that the catalytically active center consists of Ni(IV) or Co(III) atoms with a d^6 -electronic configuration, which is provided by hydrogen occluded into the active component matrix.

The key problem for understanding the mechanism of HDS catalysis seems to be the Ni (Co) electronic state in the active component composition of the sulfide HDS catalysts. For many years we have found [23,24] that Ni2p and Co2p lines in the X-ray photoelectron spectra of the sulfide Ni(Co)–Mo(W) catalysts, both bulk and supported on alumina, silica or carbon, are shifted towards

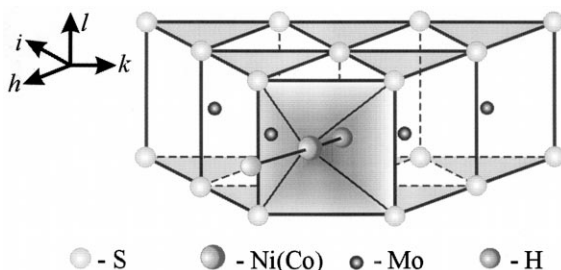


Fig. 2. Structure of the active component of the sulfide HDS catalysts with the occluded hydrogen atom and adsorbed H_2S molecule.

higher values of binding energy by 1.0–0.5 eV as compared with highly dispersed binary sulfides of these metals. As was shown by the in situ XPS study [25], these data cannot be attributed to any physical phenomena, such as the lack of relaxation energy, etc. To explain the unusually high formal positive charge on Ni or Co atoms, we have suggested that the oxidative addition of dihydrogen to Ni (Co) occurs during the catalyst sulfiding [26]. Ab initio calculations have shown that such oxidative addition is thermodynamically favorable, because it stabilizes the Ni(IV) and Co(III) d^6 electronic state. A dihydrogen molecule is assumed to dissociate on the Ni (Co) atom yielding an “occluded” H_0 located under the Ni (Co) atom in the center of the trigonal sulfur prism. The H_2S adsorption on the active center favors stabilization of the active Ni(IV) and Co(III) d^6 state [27,28]. Important, that the sixth coordination sites of these atoms cannot be “empty”, they are always occupied with adsorbed atoms or molecules (Fig. 2). The other significant conclusion was drawn from the quantum-chemical investigations [27,28]: the electron density from Ni(IV) or Co(III) atoms is transferred to the neighboring S atoms, but not to the adjacent Mo atoms, as might be expected. Therefore, we did not observe any changes in the Mo3d line position during thermal treatments of sulfide catalyst in an XPS spectrometer chamber as was discussed earlier [25].

3. Participation of anion vacancies in the catalytic cycle of the C–S bond hydrogenolysis reaction

Anion vacancies can be formed on the surface of sulfide particles after the interaction of the surface S atoms with H_2 at elevated temperature and their removal in the form of H_2S . Just these anion vacancies are considered to play a role of catalytically active centers and this hypothesis is widely spread in the literature [29]. Evidently, this belief stems from the concept of the decisive role of the binding energy of surface oxygen in oxidation reactions by oxide catalysts which was developed in early 1970s. The bond energy model, advanced by Topsoe et al. [15] and Byskov et al. [29], seems to be in the frame of this general concept. The authors of this model have inferred that due to the strong Co–Mo interaction in the active component of HDS catalysts, the metal–sulfur bond is much weaker than that in binary sulfides of both Mo and Co. This model, based on the fully self-consistent DFT calculations [29], suggests that the main role of the promoter atom is to create more vacancies which behave differently than those in unpromoted MoS_2 .

One of the main arguments to support this hypothesis is considered to be thermo-programmed experiments in hydrogen flow (see, e.g., Ref. [15] and references therein). This procedure is called “thermo-programmed reduction”, but to our mind, in a temperature range of 100–400°C no

reduction of the sulfide species occurs and appearance of H_2S in the gas phase seems to be resulted from removal of H_2S adsorbed on the active centers [13,30]. The circumstantial evidences favoring this suggestion can be found, e.g., in Ref. [31].

The mobility of surface sulfur can be measured with radioisotope tracer method using radioactive H_2 ^{35}S -labeled molecules as it is generally accepted in oxide catalysts in relation to ^{16}O – ^{18}O hetero-exchange [3]. A good correlation between the catalyst activity in the HDS reaction and the rate of isotope H_2 ^{35}S hetero-exchange was found, e.g., in Refs. [32–34]. As was shown, the rate of hetero-exchange exceeds considerably the rate of catalytic HDS reaction.

In the past we have also studied the H_2 ^{35}S hetero-exchange [35] using the highly dispersed sulfide catalyst prepared via organo-metallic complexes. Yet we did not find a correlation between the catalyst activity and the rate of exchange. Moreover, if one compares the temperature dependencies of both processes (Fig. 3), we may observe a very interesting picture. As one can see, the rate of hetero-exchange occurring at 300°C (the total pressure of H_2S is 4×10^3 Pa) exceeds that of thiophene hydrogenolysis (the total pressure of hydrogen is 2×10^6 Pa) by more than one order of magnitude. Taking into account the first order of the thiophene hydrogenolysis rate constant in relation to hydrogen, one may predict, that the rate of thiophene hydrogenolysis will be at least two orders of magnitude lower at low pressure. Therefore, the difference between the rates of both reactions will be considerably higher.

Moreover, the hetero-exchange between the labeled H_2S and the surface of sulfide (Ni,Mo) catalysts occurs at a low temperature with a very high rate and a low activation energy. Under these conditions, no HDS reaction is observed because its activation energy increases considerably at a low temperature (Fig. 3). As was mentioned earlier [13], the rate of hetero-exchange with the surface of Mo and W sulfide catalysts decreased, the amount of sulfur removed during the thermo-programmed reduction did not change after addition of Ni to these catalysts, while the catalysts activity increased significantly. Hence, one may conclude that the catalytic reaction and H_2S hetero-exchange occur simultaneously and independently on the surface of sulfide catalysts under conditions of the catalytic reactions following the different mechanisms.

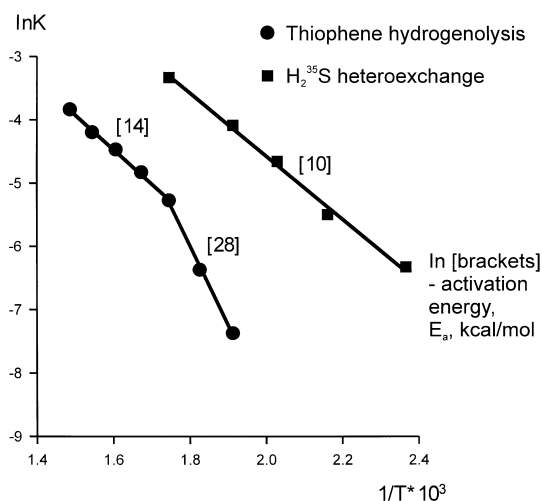


Fig. 3. Temperature dependencies of the rate of thiophene hydrogenolysis and isotope H_2 ^{35}S hetero-exchange over the sulfide (Ni,Mo) catalysts.

Let us recall very shortly some other arguments mentioned in [13]:

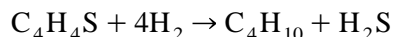
- thermodynamic calculations, made in the frame of the method of interacting bonds by Yermakov et al. [36], have shown, that the anion vacancies formation is a thermodynamically unfavorable process;
- in situ measurements of the MoS₂ single crystal conductivity made by Wise [37] have shown, when concentration of the anion vacancies increases, the catalyst activity decreases;
- semi-empirical molecular orbital calculations demonstrated in Ref. [38] have shown that in order to create anion vacancy, the activation energy over 5 eV is needed.

So, the above arguments demonstrate the participation of anion vacancies in the catalytic cycle to be the intrigue problem under question.

4. Concerted mechanisms of thiophene hydrogenolysis over sulfide catalysts of different composition

Before studying the molecular mechanism of the C–S bond hydrogenolysis reaction, at the Borekov Institute of Catalysis the problem of preparation of the highly active sulfide catalysts with rather homogeneous composition of the active component was solved. Initially π -allyl, or alkoxide, or acetylacetonate complexes were used to prepare the silica supported precursors of sulfide catalysts [39], then the aqueous solutions of metal complexes were used to prepare alumina, silica, or carbon supported sulfide catalysts [40]. In all cases, the activity of these catalysts in the model reaction of thiophene hydrogenolysis exceeds considerably the activity of catalysts prepared via conventional method of impregnation. All sulfide catalysts were characterized with different physical and chemical methods [13].

The reaction of thiophene hydrogenolysis was carried out in a flow set-up with a fix-bed reactor under hydrogen pressure of 20 bar. The reaction mixture contained hydrogen, cyclohexane, and thiophene with the molar ratio 2200:9:1. After the catalyst loading into the reactor, it was treated with a reaction mixture at 400°C up to the steady-state level of catalyst activity, then the temperature was allowed to decrease to the desired one. The first reaction order with respect to thiophene is observed in all cases, therefore the catalyst activities were compared by the rate constant of the first order. The reaction follows the scheme:



that is, no possible intermediates, such as tetrahydrothiophene or butadiene, were detected in the gas phase at the steady-state catalyst activity. One may object to large excess of hydrogen, when the possible intermediates can be readily hydrogenated at fast rates. Besides, in literature one can find THT and butadiene to be detected in the gas phase. Therefore, we have carried out a series of special experiments, when in the same installation, under the same reaction conditions and over the same catalysts, profound amounts of THT were detected, but the sulfide monometallic catalysts were preliminary reduced with hydrogen at 400°C [41]. Butadiene was found in the case of zeolite containing catalysts, when metallic particles, which were not sulfided with the reaction mixture, was possible. The presence of THT and butadiene in the gas phase means that the rate of their hydrogenation is comparable with the rate of thiophene transformation. In other words, if these intermediates are desorbed from the catalyst surface, they should be detected in any case.

The same is true for the sulfide catalysts having the active component structure similar to that of typical HDS catalysts [42]. Despite the very low level of catalytic activity of the sulfide (Ni,Nb) (synergism), (Ni,Re) (antagonism) and (Cu,W) (antagonism as well) catalysts no intermediates were detected in the gas phase as well [13,43,44].

Moreover, when THT was used as a substrate, the rate of its transformation was lower in comparison of thiophene hydrogenolysis. One should be stressed, that both reactions were carried out in the same installation, under the same reaction conditions and over the same catalysts [45,46]. We believe, that in the last case we observed very interesting phenomenon, which could be interpreted as follows. Let us suppose, that the reaction of thiophene hydrogenolysis occurs via intermediate hydrogenation of the thiophene ring and the formed THT is strongly adsorbed at the active center and does not appear in the gas phase because of the high heat of adsorption [28,47]. Enthalpies in Fig. 4 are roughly evaluated and can be defined more carefully, though they do not influence the final conclusion. From comparison of schemes of both reaction, it follows that only one stage gives an additional heat efficiency — that is, the enthalpy of the thiophene ring hydrogenation. Therefore, we believe that just this energy, accumulated in the active center, is effectively used in the catalytic cycle resulting in the higher rate of thiophene hydrogenolysis as compared to the THT one. Undoubtedly, this unexpected experimental phenomenon requires further additional investigation and understanding. In any case, this phenomenon gives a strong argument in favor of the concerted mechanism of these reactions.

Another parameter typical for the concerted mechanism is the activation energy. Earlier we have demonstrated many times that the temperature dependencies of thiophene hydrogenolysis have an inflection point in the vicinity of 300°C [13]. At this temperature, E_a decreases from 28 to 14 kcal/mol for all bimetallic sulfide catalysts. After addition of F or P to these catalysts, E_a decreases to 16 and 7 kcal/mol, respectively, in both temperature regions, while the inflection point does not change [48]. Moreover, the same inflection point at the same temperature was observed for THT hydrogenolysis [45]. This characteristic of the Arrhenius relationship was observed for all types of bimetallic sulfide catalyst, including nonporous massive Ni/WS₂ and Ni/MoS₂, regardless the

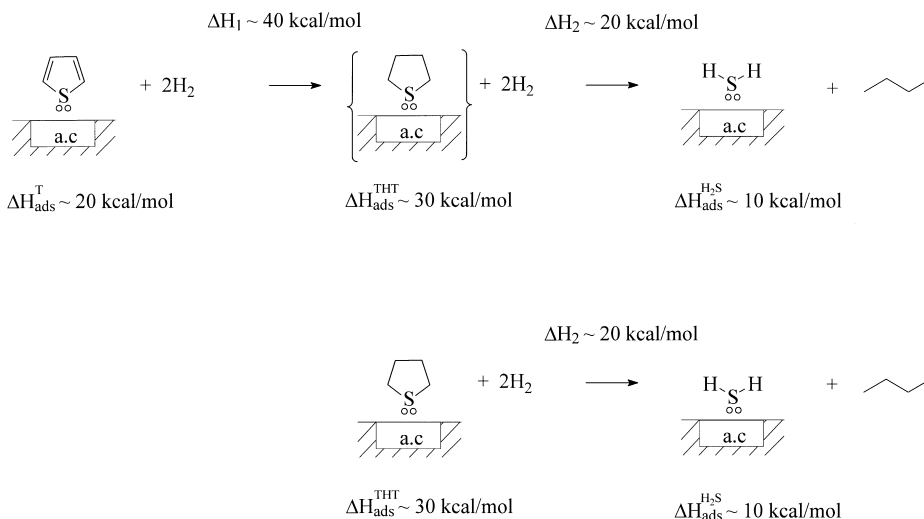


Fig. 4. Schemes of the catalytic reactions of thiophene and THT hydrogenolysis mediated by the same sulfide catalysts, in the same installation and under the same reaction conditions.

porous structure and the size of the catalyst grains. Therefore, a decrease in E_a with the increasing temperature cannot be explained by the reaction transition to the region of diffusion restrictions. The reason is most likely resulted from a change in the rate-limiting step. The low activation energies (7–11 kcal/mol) are also observed for thiophene hydrogenolysis over low active (Ni,Nb), (Ni,Re) and (Cu,W) sulfide catalyst whose active component represents a structural analog of the active component of HDS catalysts [43,44].

Let us consider now the mechanism of the thiophene hydrogenolysis reaction mediated by the sulfide bimetallic catalysts. So, the active component of the HDS catalysts is considered to be an electroneutral macromolecule (see its fragment in Fig. 5). This picture is represented at the real interatomic distance scale, therefore, the ionic and covalent radii of all sulfur atoms are different according to the literature data. The active sites, Ni or Co atoms at the edge plane of the single slab of the active component, are occupied with the adsorbed H_2S molecule.

We remember that the active center of HDS catalysts consists of Ni(IV) or Co(III) atoms with an occluded hydrogen (Fig. 2). The electron deficient Ni or Co atoms with a d^6 -electronic configuration and two unoccupied orbitals can be considered as Lewis acid centers, which are able to absorb any donor molecules, like H_2S , thiophene, THT, etc. As mentioned above, the additional electron density appears on S atoms bound to Ni(IV) and Co(III) due to the electron transfer from the central atoms [25,27]. This means that these atoms can be considered as the Lewis base centers. An adsorbed H_2S molecule can be supplanted with thiophene because of higher heat of adsorption [28,47]. As shown in Ref. [38], at η^1 -coordination of thiophene molecule to the coordinative unsaturated Mo atom in the cluster modeling the active component, a charge transfer takes place from the sulfur atom of thiophene molecule to MoS_2 . Evidently, one may suggest that the same process of electron transfer

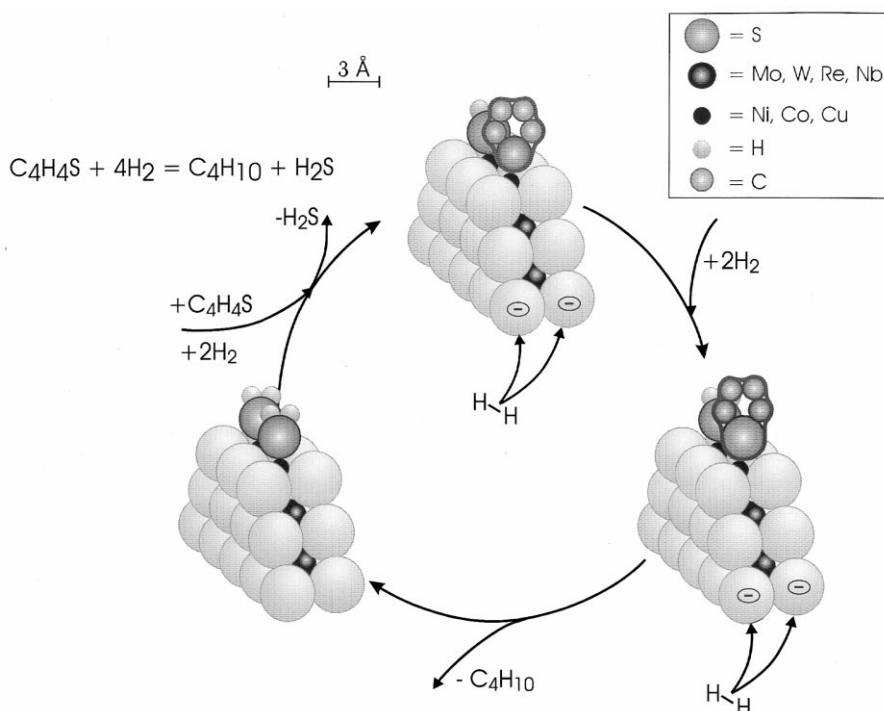
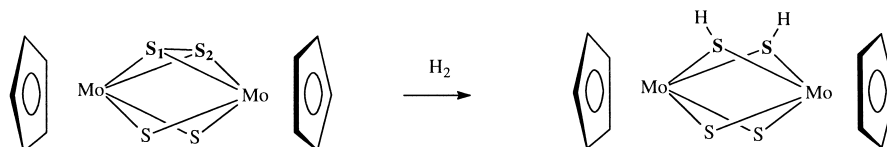


Fig. 5. Concerted mechanism of thiophene hydrogenolysis mediated by bimetallic sulfide catalysts having similar structure with the active component.

occurs at coordination of thiophene molecule to Co or Ni atoms in the active component. If so, an additional negative charge will appear on the electroneutral macromolecule of the active component. Because all valence bonds inside of the active component are saturated, the excess negative charge is likely to be centered on the coordinatively unsaturated S atoms enframed the electroneutral macromolecule of the active component. Compensation of this charge may be possible by dissociative adsorption of the dihydrogen molecule. The terminal sulfur atoms, enframed the electroneutral macromolecule of the active component and carried an excess negative charge, can be considered as Lewis base centers, which supplies electron density to the vacant antibonding σ^* — orbital of dihydrogen molecule. This process results in the homolytic splitting of the dihydrogen molecule. The activated hydrogen is transferred to the adsorbed thiophene molecule via the system of chemical bonds such as bridged S atoms. We suggest that the excess negative charge is delocalized over all terminal sulfur atoms, therefore, the activation of hydrogen may occur rather far from the sites of the thiophene activation.

As a model of the dissociative adsorption of dihydrogen on the terminal S atoms, the dinuclear sulfido-bridged molybdenum clusters, like $(C_5H_5)Mo(\mu-S)_2(\mu-S_2)Mo(C_5H_5)$,



can be considered. As was shown by Rakowski DuBois et al. ([49,50] and references therein) dihydrogen reacts with a $(\mu-S_2)$ -bridge under mild conditions to give two bridging hydrosulfide ligands. These $(\mu-S_2)$ -ligands are very reactive towards unsaturated hydrocarbons [51]. To our mind, two kinds of the bridged sulfur atoms in these complexes can serve as a beautiful model of sulfur bonding in the MoS_2 -like system: an Mo–S–Mo bridge seems to be an analog of the basal sulfur bonding because of saturation of both valence bonds in sulfur atoms, but Mo– (S_2) –Mo bridges are simulating the edge sulfur atoms, because the direct S–S bond presupposes a π -interaction between these atoms. The coordinatively unsaturated S atoms in the edge plane of the MoS_2 macromolecule should have an electronic interaction between S–S atoms.

The theoretical studies of Mo_xS_{2x} -clusters [52], simulating the active component of HDS catalysts, have shown that the addition of a dihydrogen molecule to two adjacent bridging sulfides is a thermodynamically and kinetically feasible process, because of the unpaired electron spin, directed between the sulfide atoms, is built up. The bridged sulfur atoms form an $(S_2)^{n-}$ group (n is between 1 and 2) with two uncoupled electrons. The presence of $(S_2)^{2-}$ groups in MoS_2 was shown with Raman spectroscopy [53]. Note, that dissociation of H_2 cannot occur on a single S atom [52], and the homolytic splitting of the dihydrogen molecule becomes possible just on the bridging $(S_2)^{2-}$ groups. In this case the electronic charge transfer between S atoms and the H_2 antibonding σ^* orbital may occur, thus facilitating the H_2 dissociation. The four centered mechanism of H_2 activation proposed in Ref. [52] does not presuppose the Mo–S bond to be broken.

The hydrogenation of the thiophene molecule at the first step of HDS reaction results in the destruction of the π system of the aromatic ring and appearance of the additional electron pair on the S atom. Because THT is more basic than thiophene, it does not desorb into the gas phase. Again, the

electron density from the S atom of THT is transferred to the active component and localized on the terminal sulfur atoms. This is a driving force for the dissociative adsorption of dihydrogen. Thereupon the activated hydrogen is transferred to the adsorbed THT molecule and the process is accomplished with C–S bond scission and butane (or butene) desorption into the gas phase.

As one can see, the mechanism of thiophene hydrogenolysis may be easily described with no disruption of the electroneutrality principle and without consideration of the anion vacancies participation in the catalytic cycle. Formally, this mechanism belongs to the acid–base catalysis and can be realized on the bimetallic sulfide catalyst, whose active component is crystallized in the structure typical for the active component of HDS catalysts: in spite of very low reaction rates, the thiophene hydrogenolysis reaction is characterized with low activation energy and high selectivity towards the reaction products. A possible nature of synergism and antagonism in these catalytic systems can be explained with either a very strong (or weak) interaction of the thiophene molecule with the active center, or differences in the electronic interaction of the Ni (Cu, etc.) atoms with the disulfide matrix, or difficulties with dihydrogen activation, or some another factors demanding the experimental evidence. This problem is open for discussion.

5. Summary and conclusions

The definition of acid–base catalysis, as applied to the HDS reaction, results from the corner-stone standpoint of the intermediate chemical interaction of the reactive molecule (Lewis base, donor of electrons) with the definite active centers of the solid catalysts (Lewis acid, acceptor of the lone electron pair). This offers an outstanding opportunity to present the experimental data of catalysis (heterogeneous, homogeneous and enzyme) from a unified viewpoint. Initially, an active component of the sulfide catalysts can be represented as an electroneutral macromolecule of the sulfide bimetallic species (SBMS) covered with the adsorbed H_2S to prevent the deactivation of the active centers (solvated effects in homogeneous catalysis is its analog). There exists a labile equilibrium between the surface sulfur atoms and the sulfur atoms including the composition of S-containing molecules of the gas (or liquid) phase. One can consider that during a catalytic cycle, a thiophene molecule builds one chemical bond with the active center — that is, Ni(IV) or Co(III) with a d^6 -electron configuration, by supplementing the H_2S molecule adsorbed. This is the way how catalytical active complex is formed. An excess negative charge of the latter provokes the dissociative adsorption of dihydrogen resulting in the homolitic splitting of the H–H bond. The concerted mechanism becomes possible due to the synchronous transfer of electrons and the activated hydrogen in opposite directions through the system of chemical bonds formed by terminal and bridged sulfur atoms enframed the active component. The enthalpies of exothermic reactions of the molecule adsorption and thiophene ring hydrogenation are accumulated in the active component and effectively used for the exothermic reaction of C–S bond scission. This provides low activation energies of the total catalytic reaction.

Acknowledgements

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