

# An unexpected phenomenon in heterogeneous catalysis: oxidative addition of hydrogen to the sulfide catalysts

A.N. Startsev\*, I.I. Zakharov, V.N. Parmon

*Boriskov Institute of Catalysis, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia*

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## Abstract

The paper summarizes experimental and theoretical evidence of an oxidative addition of hydrogen to the active metal (Ni or Co) in the active component of the sulfide HDS catalysts—a new phenomenon unknown to date in heterogeneous catalysis. Several aspects are discussed: thermodynamics of the oxidative addition of hydrogen; possible mechanism of dihydrogen activation by sulfide catalysts; electronic state of the active metals Ni(IV) and Co(III) with  $d^6$ -electron configuration; reversibility of the oxidative addition and reductive elimination of hydrogen at high temperature; sites of hydrogen localization inside the active component matrix; spectroscopic evidence on the existence of “occluded” hydrogen; a strong interaction of the occluded hydrogen with the active component matrix; a new version of the catalytic cycle of thiophene hydrogenolysis.

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## 1. Introduction

Hydrogen is the main “personage” in the petroleum hydroprocessing. Despite a widely accepted opinion that both the hydrogen molecule and its atomic or ionic fragments are nicely characterized in the theoretical and experimental practice, the real mechanism of hydrogen activation on the sulfide hydrotreating catalysts is not still recognized. This results from the lack of appropriate physico-chemical methods for the in situ investigation of the processes of hydrogen adsorption and activation. Hence, it is worth while to search for an analogy between heterogeneous and homogeneous

systems where the mechanisms of hydrogen activation are sufficiently well investigated by the NMR spectroscopy and the related physico-chemical methods.

In our paper the following points are discussed:

1. thermodynamics of the oxidative addition of hydrogen to a metal atom existing in a non-zero oxidation state;
2. a possible mechanism of the molecular hydrogen activation on the sulfide catalysts;
3. the electronic state of the Ni and Co atoms in the active centers of bimetallic sulfide species which are able to adsorb the electron donor molecules;
4. reversibility of the oxidative addition and reductive elimination of hydrogen at high temperatures evidenced by the in situ X-ray photoelectron spectroscopy;

\* Corresponding author.

*E-mail address:* startsev@catalysis.nsk.su (A.N. Startsev).

5. possibility of a stabilization of the hydrogen atoms inside the matrix of sulfide bimetallic species and probable sites of its localization;
6. spectroscopic evidence of the existence of the “occluded” hydrogen;
7. a strong interaction (a high thermal stability) of the occluded hydrogen with the active component matrix, which is evidenced by a temperature-programmed technique;
8. the mechanism of HDS catalysis including electronic interactions of a reactive molecule and the active metal atom.

Our considerations will be based on the following corner-stone standpoints in understanding the chemical catalysis as a natural phenomenon:

- Dihydrogen is a unique molecule which is able to serve as both a reducing agent and an oxidant under the *same* reaction conditions.
- There is a profound identity in the structure of the catalytic active sites and in the mechanisms of their functioning in homogeneous, heterogeneous and enzyme catalysts [1,2].
- Because of the lack of sensitive physical methods (like multinuclear NMR spectroscopy in homogeneous catalysis) to investigate in situ adsorption and transformation of the reactive molecules on the surface of *real* catalysts under the *real* catalytic conditions, we are obliged to search for respective analogies in homogeneous catalysis to simulate understanding of the surface reactions.
- The oxidative addition of hydrogen to a metal center is a key step in many, if not all, transition metal catalyzed homogeneous reactions involving H<sub>2</sub>.

## 2. Thermodynamics of the oxidative addition of hydrogen to a metal atom existing in a non-zero oxidation state

In homogeneous catalysis, hydrogen activation may follow three possible mechanisms: an oxidative addition, a homolytic splitting, and a heterolytic splitting [3]. Hydrogen is indeed known to situate simultaneously in the first and in the seventh groups of the Mendeleev periodic table, which reflects its properties as both a reducing agent and an oxidant.

A reaction of oxidative addition of hydrogen was discovered almost 40 years ago by Vaska and DiLucio

[4]. They demonstrated that after the hydrogen addition a formal oxidation state of the initial form of the Ir(I), d<sup>8</sup> cation increases by two and electronic configuration of the iridium cation transforms into Ir(III), d<sup>6</sup>.



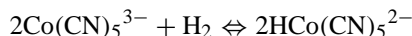
Later a lot of extra examples appeared in literature [5]. Here, we demonstrate only two additional examples of the oxidation of metal cations with a high formal oxidation state: Os(II), d<sup>6</sup> into Os(IV), d<sup>4</sup> [6]:



and Mo(II), d<sup>4</sup> into Mo(IV), d<sup>2</sup> [7]:



In the both cases, the formal oxidation state of a metal cation increases by two while its coordination number increases simultaneously by two as well. It is so called the two-electron hydrogen oxidative addition. The one electron oxidative addition is well known too, e.g. a transformation of Co(II), d<sup>7</sup> into Co(III), d<sup>6</sup> [8]:



This case is especially typical for the square-planar complexes, which have a strong tendency to the oxidative addition. The best example is the first step of the active center formation in the Wilkinson' olefin hydrogenation catalysts [9]. Important that the oxidative addition occurs very easy if the coordination sphere of an atom contains electron donor ligands like PPh<sub>3</sub>, PBu<sub>3</sub>, etc.

In heterogeneous catalysis, adsorption and activation of molecular hydrogen over the metal surface seems to be an analogue of the oxidative addition to the metal atom (Fig. 1). Hence the mechanism of the hydrogen activation seems to be the similar one as well. In the transient state, the σ bond H–H serves as a donor in relation to the vacant d-orbitals of a metal. A back π-donation occurs from the occupied d-orbital of the metal with π-symmetry over the antibonding σ-orbital of hydrogen. Corresponding thermochemical estimations are given in Table 1. That means that oxidative addition of hydrogen should be an exothermic reaction with low activation energy (<10 kcal/mol).

In the case of sulfide catalysts, a heterolytic activation of hydrogen can take place. According to

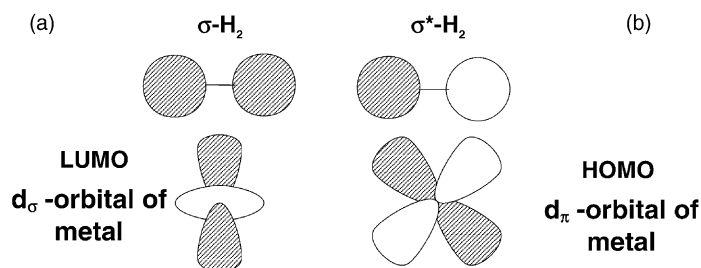


Fig. 1. A molecular orbital scheme of homolytic activation of the dihydrogen molecule on transition metal atoms.

thermochemical estimations and quantum–chemical calculations by Rodriguez [10], the heterolytic activation of hydrogen is also thermodynamically favorable and occurs as an one-electron addition of hydrogen resulted in the formation of a surface metal hydride. From this consideration an important conclusion can be drawn: *dihydrogen activation on sulfide catalysts may be of the same efficiency as that on metals.*

### 3. A possible mechanism of the molecular hydrogen activation on sulfide catalysts

As a model of the dissociative adsorption of dihydrogen on the terminal S atoms, some dinuclear sulfido-bridged molybdenum clusters like  $(\text{C}_5\text{H}_5)\text{Mo}(\mu\text{-S})_2(\mu\text{-S}_2)\text{Mo}(\text{C}_5\text{H}_5)$  one can consider:

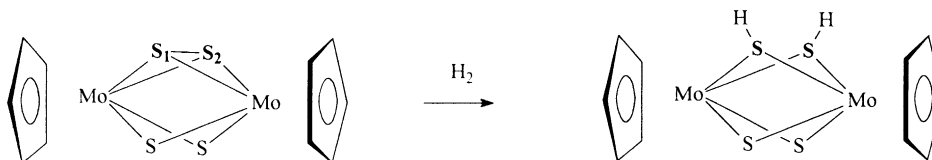


Table 1  
Thermochemical estimations of dihydrogen activation on metals and sulfides

Homolytic dihydrogen activation on metal complexes and surfaces [5]	
Bonding energy of H–H (kcal/mol)	104
Bonding energy of M–H (kcal/mol)	60–70
The experimental value $\Delta H^\circ$ (kcal/mol)	–(16–36)
The estimated value $\Delta S^\circ$ (cal/(mol K))	–35
For $T = 300\text{ K}$	
$-T\Delta S^\circ$ (kcal/mol)	+10
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (kcal/mol)	–(6–26)
Heterolytic dihydrogen activation on sulfide catalysts [10]	
Bonding energy of M–H (kcal/mol)	80–90
Bonding energy of S–H (kcal/mol)	50–60
The experimental value $\Delta H^\circ$ (kcal/mol)	–(26–46)
The estimated value $\Delta S^\circ$ (cal/(mol K))	–30
For $T = 600\text{ K}$	
$-T\Delta S^\circ$ (kcal/mol)	+18
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (kcal/mol)	–(8–28)

As was shown by Rakowski DuBois ([11,12] and refs. therein), dihydrogen reacts with the  $(\mu\text{-S}_2)$ -bridge under mild conditions to give two bridging hydrosulfide ligands. These  $(\mu\text{-S}_2)$ -ligands are very reactive towards unsaturated hydrocarbons. To our mind, two kinds of the bridged sulfur atoms in these complexes can serve as a beautiful model of the sulfur bonding in  $\text{MoS}_2$ -like system: a Mo–S–Mo bridge seems to be an analog of the basal sulfur bonding because of saturation of both valence bonds in the sulfur atoms, while Mo– $(\text{S}_2)$ –Mo bridges simulate the edge sulfur atoms, because the direct S–S bond presupposes a  $\pi$ -interaction between these atoms. The coordinatively unsaturated S atoms in the edge plane of the  $\text{MoS}_2$  macromolecule should have an electronic interaction between S–S atoms. A theoretical and experimental evidence of a homolytic dihydrogen dissociation on the Mo– $(\text{S}_2)^{2-}$ –Mo units was given by Sanchez Delgado [13]. This possibility was also considered by Sierraalta and Ruetter [14].

#### 4. Reversibility of the oxidative addition and reductive elimination of dihydrogen at high temperatures as evidenced by the in situ X-ray photoelectron spectroscopy

A crucial point for understanding the nature of catalytically active species is specificity of the electronic structure of active metal atoms. A direct experimental investigation of the formal oxidation state of metal atoms is allowed by the X-ray photoelectron spectroscopy (XPS). However, when being applied to the highly dispersed supported catalytic systems including supported sulfide catalysts, this technique meets some restrictions. Indeed, many papers describe XPS studies of sulfide catalysts (see e.g. [15] and refs. therein). It has been found that in the bimetallic (e.g. Ni, Mo, Ni, W or Co, Mo) sulfide catalysts the electronic state of Mo (W) corresponds to that in the both bulk and supported MoS<sub>2</sub> (WS<sub>2</sub>), while the state of Co (Ni) remains the subject of discussion. Depending on the way of the catalyst preparation and the activation procedures, the Co or Ni atoms in the sulfide catalysts were found to be either in an oxide surrounding or in a metallic state, or in the form of sulfide species like Co<sub>9</sub>S<sub>8</sub>, or in some any others. The main reason for these debates is a very complicated profile of the Co and Ni XPS lines, which is caused by heterogeneity of surface species. Nevertheless, based on a generally accepted model of the active component of HDS catalysts, we have to find a certain distinctive feature of the Ni (Co) electronic state in the active component matrix (in comparison with binary sulfides of these elements), because we should expect a chemical interaction between the Ni (Co) and Mo atoms. The increase in binding energies (BE) of Ni (Co) in bimetallic sulfide catalysts in comparison with the binary sulfides of these metals was found in [16–19], but this shift was either attributed to the physical phenomenon, like sample charging [17], or not discussed at all.

We have found some years ago that, in the sulfide bimetallic catalysts prepared via metal complex precursors, the position of the Ni (Co) lines in the X-ray photoelectron spectra is shifted to the higher values of BEs in comparison with those in binary sulfides of the same metals [20]. It was especially strange, because we had to expect that at high temperature and high hydrogen pressure, the Ni or Co atoms must be reduced

to form a lower oxidation state. Nevertheless, we observed an opposite effect, which regularly reproduces itself in different catalytic systems: silica [20], alumina [21,22] and carbon [23] supported bimetallic sulfide catalysts, bulk sulfides Ni/WS<sub>2</sub> [24,25], Co/MoS<sub>2</sub>, Co/WS<sub>2</sub>, Ni/ReS<sub>2</sub>, Cu/WS<sub>2</sub> [25].

Here we have to exclude an argument, which arises sometimes in discussions of the sulfide catalyst properties: in the catalysts prepared via metal complex precursors the structure of the active component may be different from that of the typical HDS catalysts prepared via conventional methods. However, comprehensive studies of these catalysts with modern physico-chemical methods (the results are summarized in Reviews [26,27]) have shown an identity in the active component structure and the catalytic properties of the catalytic systems prepared both via metal complex precursors and by conventional methods of impregnation. At the same time, according to our studies, the catalysts prepared from the metal complex precursors are characterized by a more uniform composition of the active component. Therefore, their activity in thiophene hydrogenolysis is higher in comparison with the “standard” ones [28]. As a result of this homogeneity, the Ni 2p line in the XP-spectra is narrow (Figs. 2 and 3) and its position may be interpreted more or less unambiguously.

In the alumina supported sulfide catalysts, the Mo 3d line is characterized by a narrow poorly resolved doublet with the Mo 3d<sub>5/2</sub> BE exactly as in both bulk and highly dispersed MoS<sub>2</sub> (Fig. 2). The position of this line does not change after heating in the spectrometer chamber in vacuum or in the atmosphere of (H<sub>2</sub> + H<sub>2</sub>S). For the Sibunit supported catalysts (Fig. 3), this line is a well-resolved doublet, but its position is shifted towards higher BEs. This shift seems to result from the chemical interaction of the active component with the support surface [26]. Of importance is that the line position does not change after the in situ heating neither in vacuum, nor in hydrogen, nor in the (H<sub>2</sub> + H<sub>2</sub>S) atmosphere.

At the same time, the Ni 2p line changes its position essentially after the in situ thermal treatments (Figs. 2 and 3). The Ni 2p line of the freshly ex situ sulfided bimetallic catalysts are shifted by 1.0 eV to higher BEs with respect to the highly dispersed NiS/Al<sub>2</sub>O<sub>3</sub>. In the Sibunit supported bimetallic sulfide catalysts this line is shifted at the same direction even more. After

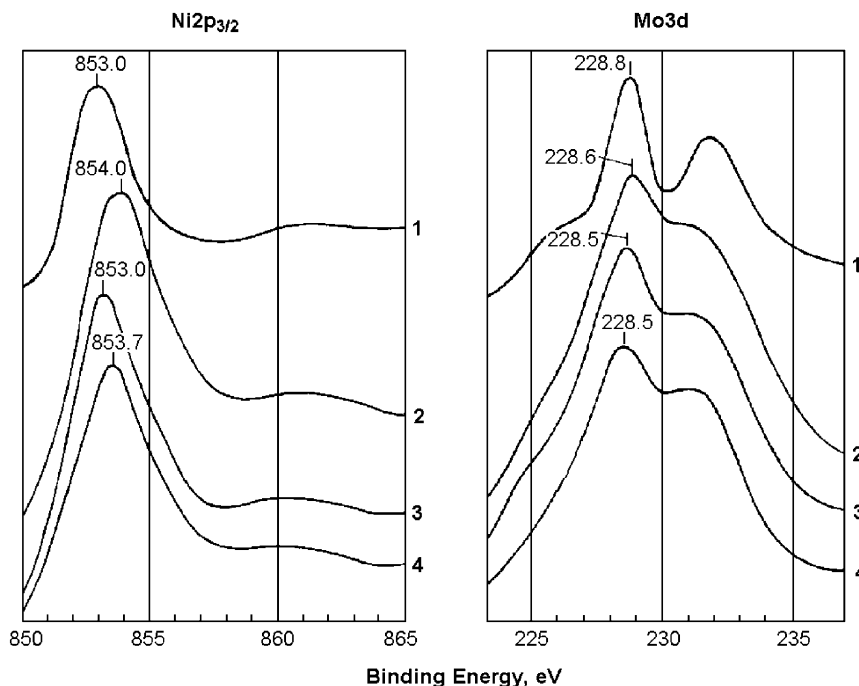


Fig. 2. XPS data on the electronic state of the Ni and Mo atoms in the active component composition of the sulfide (Ni, Mo)/Al<sub>2</sub>O<sub>3</sub> catalysts. (1) NiS/Al<sub>2</sub>O<sub>3</sub> catalyst and mechanical mixture (MoS<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>); (2) the (Ni, Mo)/Al<sub>2</sub>O<sub>3</sub> catalyst is sulfided ex situ at 400 °C; (3) the previous sample is evacuated in situ at 300 °C until residual pressure of  $5 \times 10^{-9}$  Torr; (4) the previous sample is sulfided in situ in the (H<sub>2</sub> + H<sub>2</sub>S) mixture at 300 °C [23].

sulfide catalysts vacuuming at 300–500 °C to residual  $10^{-10}$  Torr, the Ni 2p line is shifted by 1.0–1.2 eV to the lower BEs for both catalysts. The magnitude of the shift exceeds considerably the BE measurements accuracy and corresponds to the Ni 2p line position in the highly dispersed NiS. Note that this line position does not change after sample treatment with hydrogen at 300–400 °C. The treatment of the vacuumed sample with the (H<sub>2</sub> + H<sub>2</sub>S) mixture at 300–450 °C in the spectrometer chamber shifts the Ni 2p line by 0.5–0.7 eV back to the higher values of BEs. This change in the Ni 2p line position seems to be reversible and is observed after repeated treatments. The similar treatment of the highly dispersed NiS/Al<sub>2</sub>O<sub>3</sub> catalyst results in another regularities (for details see [23]).

Here we omit the speculations, which concern the spectra interpretation, because this was done in our recent paper [23]. But we have to stress that the observed chemical shift of the Ni 2p lines must be attributed to

a *chemical phenomenon* rather than to any physical action of radiation on the investigated pattern. Recently [29], the similar observation in the positive shift of the Ni 2p BEs was made for the bulk Ni/WS<sub>2</sub> catalysts. This is an additional argument in favor of the chemical nature of the phenomenon observed, because in this case we may exclude support effects and lack of relaxation energy in highly dispersed particles. We believe that this effect results from an unusual electronic state of Ni(IV) (or Co(III) as well).

A possibility formation of the Ni(IV) and Co(III) cations with d<sup>6</sup>-electronic configuration was demonstrated with some ab initio investigations [30–34]. According those calculations, the Ni(II) cation with the d<sup>8</sup>-electronic structure (being in the square-planar environment of the S atoms) transforms into Ni(IV) (d<sup>6</sup>) in a square-pyramidal surrounding when the H<sub>2</sub>S molecule adsorbs on the Ni cation to the fifth coordination site. The same situation is realized when the H<sub>2</sub>S molecule adsorbs on the Ni cation in the sulfide

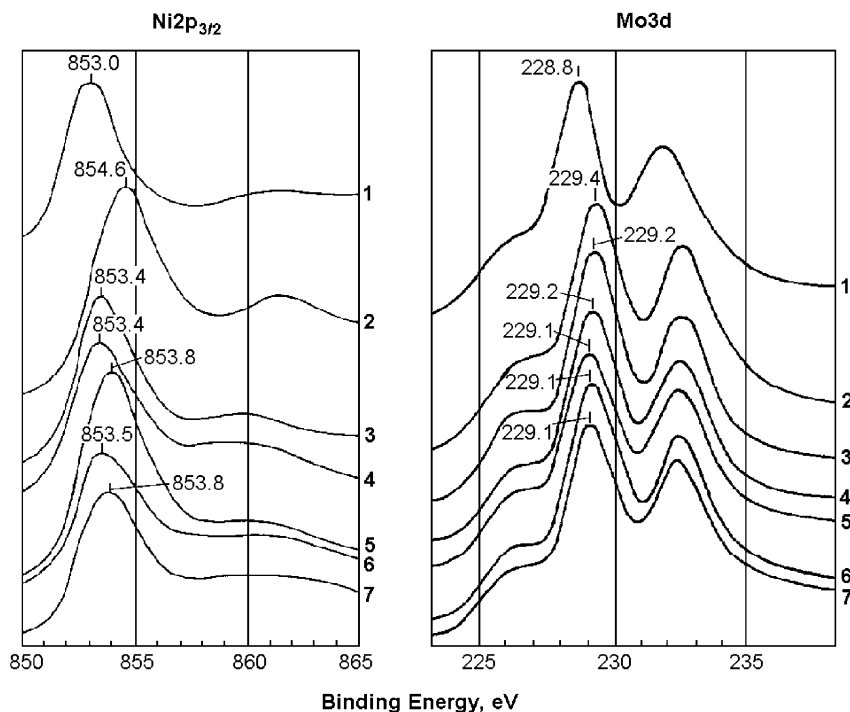


Fig. 3. XPS data on the electronic state of Ni and Mo in the active component composition of the sulfide (Ni, Mo)/Sibunit catalysts. (1) NiS/Al<sub>2</sub>O<sub>3</sub> catalyst and mechanical mixture (MoS<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>); (2) (Ni, Mo)/Sibunit catalyst sulfided ex situ at 400 °C; (3) the previous sample is evacuated in situ at 400 °C until residual pressure of  $5 \times 10^{-9}$  Torr; (4) the previous sample is reduced in situ in hydrogen at 300 °C; (5) the previous sample is sulfided in situ in (H<sub>2</sub> + H<sub>2</sub>S) at 300 °C. (6) the previous sample is evacuated in situ at 300 °C until residual pressure of  $5 \times 10^{-9}$  Torr; (7) the previous sample is sulfided in situ in (H<sub>2</sub> + H<sub>2</sub>S) at 300 °C [23].

bimetallic species. In this case, the electron density from Ni does not transfer to Mo, but is localized on the S atoms bounded to Ni.

To explain an unusually high formal positive charge of the Ni (Co) atoms, we suggested an oxidative addition of dihydrogen to the Ni or Co cations to occur during sulfiding the catalyst [32–34]. The ab initio calculations show that the oxidative addition is thermodynamically favorable and stabilizing the d<sup>6</sup>-electronic state of Ni(IV) and Co(III). The dihydrogen molecule is assumed to dissociate on the Ni atom yielding a “surface” hydrogen atom H<sub>s</sub> and an “occluded” hydrogen atom H<sub>o</sub>. The latter locates under the Ni atom in the center of a trigonal sulfur prism. The adsorption of H<sub>2</sub>S on the active center further stabilizes the active Ni(IV) d<sup>6</sup>-state. The structure of the active component with the occluded hydrogen can be represented as follow in Fig. 4.

To our mind, the active component of the sulfide HDS catalysts consists of the single slab of MoS<sub>2</sub> (WS<sub>2</sub>) with the Ni (Co) atoms being located in the edges. The Mo–Mo (3.16 Å) and Mo–S (2.41 Å) distances are typical for molybdenite structure. The Co–Mo-bond length (2.80 Å) is taken from experimental data [35]. In the MoS<sub>2</sub> single slab, the Mo atoms are known to locate at the center of a triangular prism surrounded by six sulfur atoms. The prisms are joined by an edge and form a “sandwich” in such a way that the every second prism is “empty” (contains no Mo atom). Therefore, the “empty” prism is adequate for stabilizing the hydrogen atom. Actually, if we subtract the ionic radius of S<sup>2-</sup> (1.58 Å) from the M–S distance (2.41 Å), we get the radius of the “empty” space (0.83 Å) which is a little bit larger than the H–H bond distance in the dihydrogen molecule (0.78 Å). The ab initio calculated distances Ni–H<sub>o</sub>

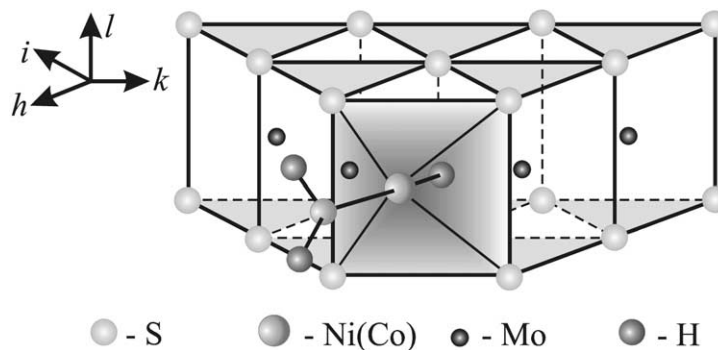


Fig. 4. An expected structure of the active component of the sulfide HDS catalysts with the occluded hydrogen atom and the adsorbed  $\text{H}_2\text{S}$  molecule.

(1.48 Å [33]) and  $\text{Co-H}_o$  (1.52 Å [34]) evidence in a covalent bonding, while the  $\text{Mo-H}_o$  bond length (1.7 Å) seems to be presupposed as a weak “agostic” interaction. The typical  $\text{M-H}$  distances in the transition metal hydrides are known to be ca 2.35 Å, while the covalent  $\text{M-H}$  bond distance is  $<1.7$  Å [36,37]. Hence, we may evidently suggest that the “actual” radius the hydrogen atom in the hole of the trigonal prism is 0.42 Å (Fig. 4). In this case, the dual nature of the hydrogen atom should be realized in an ambivalent interaction with the adjacent Ni (Co) and S atoms.

The idea of the oxidative dihydrogen addition allows a complete explanation of the observed peculiarities of the XPS data mentioned earlier. Actually, the evacuation at high temperature of the ex situ sulfided catalysts results in a *reductive elimination of dihydrogen*, therefore, we observe a shift of the Ni 2p line to the lower values of binding energy. A consecutive treatment of the same evacuated sample with the ( $\text{H}_2 + \text{H}_2\text{S}$ ) mixture at 300 °C causes the *oxidative addition of dihydrogen*, therefore, we observe a shift of this line to the higher values of binding energy. An exposure of the freshly sulfided catalysts to air results in the oxidation of occluded hydrogen, therefore, we observe reduction  $\text{Ni(IV)} \rightarrow \text{Ni(II)}$ .

An other significant conclusion was drawn from the quantum–chemical investigations [33,34]: the electron density from the Ni(IV) or Co(III) atoms is transferred to the neighboring S atoms, but not to the adjacent Mo atoms, as might be expected. Therefore, we did not observe any changes in the Mo 3d line position

during thermal treatments of sulfide catalyst inside a XPS spectrometer chamber as was discussed earlier.

### 5. Possibility to stabilize the hydrogen atom inside the matrix of sulfide bimetallic species and probable sites of its localization

Most of the papers on the HDS catalysts are devoted to studies on hydrogen sorption by  $\text{MoS}_2$ , both bulk and supported, while only few papers deal with  $\text{MoS}_2$  promoted by Ni (Co). The amount of hydrogen sorbed depends essentially on the method of the  $\text{MoS}_2$  preparation as well as conditions of the sorption, and increases considerably coming from bulk to supported samples. As a result, some confusion exists in published papers about the form and amount of the hydrogen sorbed. Therefore, the respective comparison can be made only qualitatively.

Some unusual properties of hydrogen absorbed by  $\text{MoS}_2$  were reported in the pioneered paper by Badger et al., who have shown that the amount of hydrogen sorbed by bulk  $\text{MoS}_2$  exceeds considerably a monolayer coverage of the sample [38]. Wright et al. have also shown that this amount was threefold greater than that of  $\text{N}_2$  and CO which are used for the BET surface measurement [39]. The X-ray and neutron diffraction spectroscopy data confirm the hypothesis on intercalation hydrogen between the  $\text{MoS}_2$  layers, because the c parameter of the crystal lattice is increased [40,41].

For the alumina supported  $\text{MoS}_2$ , the molar amount of hydrogen sorbed is much higher than for the bulk

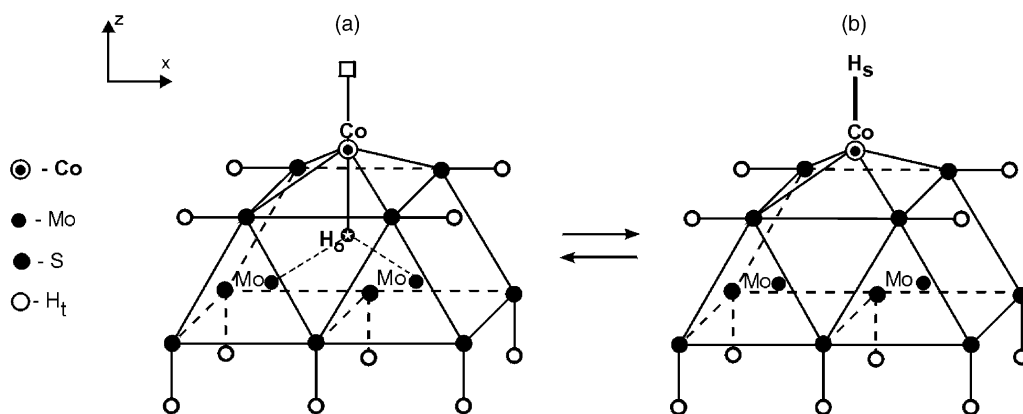


Fig. 5. A proposed quantum-chemical model of the  $(\text{H})\text{CoMo}_2\text{S}_{10}\text{H}_{10}$  cluster as an active site of the trivalent cobalt on ( $d^6$ ) in the  $\text{Co}/\text{MoS}_2$  catalysts with the occluded (a) and the adsorbed (b) hydrogen atoms.

$\text{MoS}_2$  [42–44]. Because of the lack of regular stacking of  $\text{MoS}_2$  layers in this case one can not speak about intercalated hydrogen. Thus, this phenomenon was attributed to hydrogen spillover from  $\text{MoS}_2$  particles to the support. The presence of excess hydrogen favors to the hydrogenation reactions but inhibits the  $\text{H}_2$ – $\text{D}_2$  exchange [45]. When considering this phenomenon, Anderson et al. [46] proposed the HDS reaction to occur over a  $\text{H}_x\text{MoS}_2$  catalyst.

The amount of hydrogen sorbed by both bulk and supported  $\text{MoS}_2$  can be estimated by the H–D isotopic exchange with the gas phase. Thomas et al. [47–49] showed that even at  $80^\circ\text{C}$  the amount of exchangeable hydrogen retained by the catalysts exceeds three at H per at Mo. Nickel had no significant effect on the rate of H–D-exchange or on the amount of the exchangeable hydrogen [49]. In the case of the carbon supported sulfide catalysts this amount is much higher [50]. This phenomenon was interpreted as a spillover of hydrogen to the support surface.

With this regard, it was necessary to identify different hydrogen species sorbed in the  $\text{MoS}_2$  and  $\text{Ni}(\text{Co})\text{-MoS}_2$  catalysts. As an example, one can consider tantalum–hydrogen bronze,  $\text{H}_x\text{TaS}_2$ , where the hydrogen atom is localized in the center of a trigonal prism of the sulfur atoms [51]. Blackburn and Sermon [52] assumed structures of  $\text{H}_x\text{MoS}_2$  and  $\text{H}_x\text{TaS}_2$  to be similar. Quantum-chemical calculations [46] with a semi-empirical method of molecular orbitals (ASED-MO) for a  $\text{MoS}_2$  cluster model (cluster

$\text{Mo}_7\text{S}_{24}^{20-}$ ) show that the occluded hydrogen atom  $\text{H}_o$  localized in the center of the trigonal prism  $\text{S}_6$  is stable, but the calculated binding energy is lower (37 kcal/mol) than that of the hydrogen atom adsorbed on the  $\text{MoS}_2$  surface (100 kcal/mol).

However, our calculations made by the HF, MP2, and DFT method [34] evidence both  $\text{H}_o$  and  $\text{H}_s$  states are energetically equivalent if regarded with the cluster model  $(\text{H})\text{CoMo}_2\text{S}_{10}\text{H}_{10}$  (Fig. 5). In the model, the “surface-sorbed” hydrogen  $\text{H}_s$  has been considered as a terminal H atom adsorbed on the Co atom, while the “bulk-sorbed” hydrogen is bonded to the Co atom and localized in the center of the trigonal prism of the sulfur atoms in the  $\text{MoS}_2$  unit cell. The latter hydrogen species can be called as occluded hydrogen  $\text{H}_o$ . The calculated electronic structure of Co with valent  $d_{xy}$ - and  $d_{z^2}$ -orbitals (see Fig. 5 for the coordinate system) corresponds to the oxidation state  $\text{Co}(\text{III})$  with the  $d^6$ -electronic configuration. The lowest calculated electronic states of clusters  $(\text{H})\text{CoMo}_2\text{S}_{10}\text{H}_{10}$  with either  $\text{H}_s$  or  $\text{H}_o$  was shown to be very similar in respect to total energy. The calculated entropy difference between  $\text{H}_o$  and  $\text{H}_s$  in the active center appeared to be also very small. Regarding the calculated net charges on the hydrogen atoms, one may assume that the hydrogen  $\text{H}_o$  forms a more hydride like bond (the charge on  $\text{H}_o$  is more negative) than the hydrogen  $\text{H}_s$  does, because  $\text{H}_o$  is extra bonded to two Mo atoms (see Fig. 5a). Therefore,  $\text{H}_o$  existence seems to be quite probable and reasonable. As mentioned earlier,



the occluded hydrogen atom has a covalent bond with the Ni(IV) or Co(III) cations and a “formal” covalent bonding with the Mo atom. Simultaneously, this hydrogen atom is surrounded with six sulfur  $S^{2-}$  ions. Hence, one should expect an ionic character of the S–H-bonding. This unusual state of hydrogen atoms in the surface bimetallic species seems to result from the dual nature of hydrogen as follows from its position in the Mendeleev periodic table. We may also presuppose that the excess of hydrogen in the sulfide catalysts, which is able to the isotopic H–D exchange at mild conditions [47–50], could be also attributed to the occluded hydrogen. To prove this hypothesis, direct experimental evidence must be initiated.

## 6. Spectroscopic evidence on the existence of occluded hydrogen

According to the IR data [53], the hydrogen sorption by bulk  $MoS_2$  at ambient temperature results in appearance of a broad band at  $2500\text{ cm}^{-1}$ , which splits into three ones centered at 2454, 2532 and  $2649\text{ cm}^{-1}$  after evacuation at  $400^\circ\text{C}$ . These bands were assigned to the stretching modes of Mo–SH groups. The IR data for  $WS_2$  are essentially similar. The  $^1\text{H}$  NMR measurements on  $H_xMoS_2$  are consistent with the assignment of  $H_x$  to S–H-groups [54]. The authors of [55] in agreement with the INS results concluded that besides these groups, the hydrogen atoms could also locate between the  $MoS_2$  layers.

We have calculated recently [34] the stretching and bending modes of the surface and occluded hydrogen atoms in the Co–Mo sulfide species (Fig. 5). The calculated IR spectra show that the vibrational frequency for the Co– $H_s$  bond ( $\nu = 1972\text{ cm}^{-1}$ ,  $\delta_x \approx \delta_y = 652\text{ cm}^{-1}$ ) fits the range of the experimental vibrational frequencies, characteristic of monohydride molecular complexes of Co [36] as well as hydrogen species adsorbed on the catalyst Ni/ $MoS_2$  [55]. The calculated IR spectrum shows that the vibrational frequency Co– $H_o$  ( $\nu = 1696\text{ cm}^{-1}$ ,  $\delta_x = 1764\text{ cm}^{-1}$ ,  $\delta_y = 880\text{ cm}^{-1}$ ) agrees well with a neutron Compton scattering (NCS) study of hydrogen in the Co/ $MoS_2$  catalyst [56]. Note, that the authors of [56] have concluded that the sorbed hydrogen in the Co/ $MoS_2$  catalyst is bonded to sulfur.

Earlier [33] we have calculated also the IR spectra of the  $H_s$  and  $H_o$  atoms in the Ni/ $MoS_2$  catalysts using the same cluster model  $(H_s)(H_o)NiMo_2S_{10}H_{10}$ . When comparing our calculations with the experimental spectrum of inelastic neutron scattering (INS), one can see that the bands experimentally observed at 795 and  $1895\text{ cm}^{-1}$  for the Ni/ $MoS_2$  catalysts [55] are in a good agreement with those ( $\nu_{Ni-H} = 1890\text{ cm}^{-1}$ ,  $\delta_{Ni-H(x)} = 704\text{ cm}^{-1}$ ,  $\delta_{Ni-H(y)} = 834\text{ cm}^{-1}$ ) calculated for  $H_s$  [33].

Thus, one may draw the following important conclusion: sulfide HDS catalysts perform a dissociative activation of molecular hydrogen, which may indeed be occluded in the active component matrix. This “concealed” hydrogen provides the catalytically active Co (Ni) sites with a  $d^6$ -electronic configuration.

## 7. A strong interaction of the occluded hydrogen with the active component matrix

The principal point of the hypothesis on the oxidative addition of hydrogen is that the occluded hydrogen atom has to be very strongly bonded in the active component matrix and thus, can not be released at temperatures typical for catalytic processes ( $300\text{--}400^\circ\text{C}$ ). Namely the strongly bonded hydrogen was found in [57]. We believe that the appearance of strongly bonded hydrogen results from its occlusion in the active component matrix. The main results of the temperature programmed desorption (TPD) studies of the sulfide catalysts were presented in [58]. The typical picture of the hydrogen desorptionograms from the sulfide (Co, Mo) and (Ni, Mo) catalysts is presented in Fig. 6. Here, we summarize some peculiarities of these catalytic systems.

1. In the alumina supported sulfide catalysts (both mono- and bimetallic) there are two types of hydrogen: hydrogen which is weakly bound (the desorption temperature  $200\text{--}500^\circ\text{C}$ ) and that which is strongly bound (desorption temperature above  $500^\circ\text{C}$ ).
2. After re-sulfiding of the heated catalysts with the  $H_2S$  pulses at  $400^\circ\text{C}$ , the TPH line profile for all catalysts changes drastically. First of all, we do not observe the hydrogen evolution above  $400^\circ\text{C}$ . For Co and Ni catalysts small amount of hydrogen

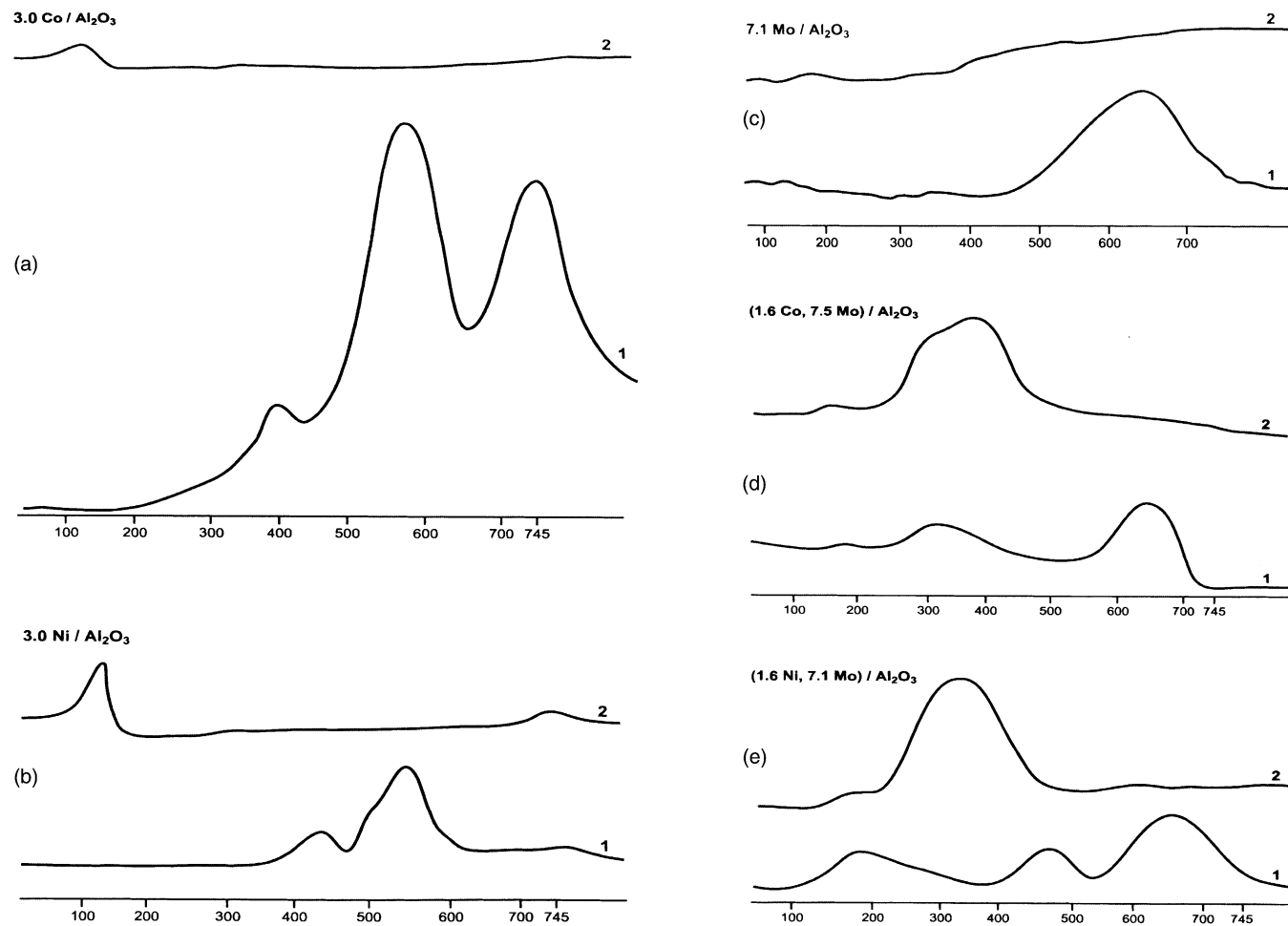


Fig. 6. Desorption thermograms of hydrogen from the sulfide catalysts: (1) freshly in situ sulfided catalysts; (2) the catalysts 1 were re-sulfided by H<sub>2</sub>S pulses at 400 °C (the temperature scale is given in degree Celsius).

was observed in the vicinity of 150 °C, while for the bimetallic sulfide catalysts a large amount of hydrogen is evolved in the range 300–400 °C. Thus, the sulfide catalysts without occluded hydrogen can be produced.

With this respect, we believe that the strongly bound hydrogen is an occluded one, because the thermal decomposition of the any transition metal hydrides completed at temperature as low as 200 °C (at the absence of hydrogen in a gas phase) [36,37], while any thio Mo complexes decompose at temperature lower than 400 °C resulted in the MoS<sub>2</sub> formation [59].

It should be stressed that nearly similar results on the hydrogen desorption were obtained by Moyes and co-workers [57]. They have also found two types of hydrogen in the Co/MoS<sub>2</sub> catalysts: those which are weakly bound (desorption temperature 150–450 °C) and strongly bound (desorption temperature above 450 °C). Of importance is that the amount of hydrogen desorbed at high temperatures strongly correlates with HDS activity. Note also, H<sub>o</sub> appears to be thermally more stable in the Co/MoS<sub>2</sub> catalysts than in MoS<sub>2</sub> ones [57].

## 8. Active center and catalytic cycle of thiophene hydrogenolysis

Regarding the results presented earlier, one can consider the Ni(II), d<sup>8</sup> and Co(II), d<sup>7</sup> ions in a square-planar sulfur environment, which might be present in real sulfide catalysts, to be not active in the HDS process. This conclusion follows from the calculated electronic structure of Ni(II) in the square-planar coordination with the sulfur atoms [29]. According to the calculations, the Ni(II) atom has one formally empty d<sub>xy</sub>-orbital above four occupied d-orbitals; therefore the expected interaction of this ion with an adsorbed H<sub>2</sub>S molecule has to be very weak. The small value of the adsorption energy, 36 kJ/mol, shows that the interaction with H<sub>2</sub>S has a polarizative (non-covalent) nature.

However, the electronic state Ni, d<sup>8</sup> or Co, d<sup>7</sup> can transform to the d<sup>6</sup>-state during the oxidative addition of hydrogen. Only this d<sup>6</sup>-electronic state is responsible for the adsorption of S-containing molecules [29]. In this case, the Ni(IV) ion has two formally empty d<sub>σ</sub>-orbitals above three occupied d<sub>π</sub>-orbitals. The com-

puted MP2 total energies for the adsorption complex with Ni(IV) in the d<sup>6</sup>d<sub>z<sup>2</sup></sub><sup>0</sup>d<sub>xy</sub><sup>0</sup>-electron configuration is lower than for divalent Ni(II), d<sup>8</sup>d<sub>xy</sub><sup>0</sup> [29]. The adsorption energy of the H<sub>2</sub>S molecule for the Ni(IV), d<sup>6</sup>-state (E<sub>ads</sub> = 82.6 kJ/mol) is greater than for the Ni(II), d<sup>8</sup>-state (see earlier). A relatively strong interaction between the H<sub>2</sub>S (or thiophene molecule as well) and the Ni(IV) or Co(III) ion can be understood in terms of an orbital overlap (Fig. 7). Two lone electron pairs n<sub>σ</sub> and n<sub>π</sub> interact efficiently with two vacant d<sub>σ</sub>(z<sup>2</sup>) and d<sub>π</sub>(xz)-orbitals of the Ni(IV) or Co(III) configuration. The H<sub>2</sub>S molecule adsorption on the Ni(IV) or Co(III) active center results in the charge transfer from H<sub>2</sub>S to the Ni (Co) and four sulfur atoms of the active component (not to the Mo atoms!), which are at the base of a pyramidal adsorption complex [29]. The calculated MP2 values of charges on the Mo atoms in Ni(II)/MoS<sub>2</sub> and Ni(IV)/MoS<sub>2</sub> (q = +0.55 and +0.58, respectively) indicate that the reduction of the Mo atom does not occur, while the oxidation of nickel (Ni<sup>2+</sup> → Ni<sup>4+</sup>) results in significant changes of the charge on the Ni atom (+0.40 → +0.97).

Note that the decisive role of Ni (Co) in the activation of S-containing molecules is under intensive development for many years, and the Ni or Co atoms are considered to not “promoters”, but the *active centers* (see e.g. [26,27] and refs. therein). Later, the key role of the Co (Ni) atoms in the activation of S-containing molecules was also demonstrated by Rodriguez et al. [60–63]. In their study, both the HDS activity and catalyst ability to interact with the S-containing molecules correlate obviously with each other. The adsorption of hydrogen on different cluster models (Mo<sub>y</sub>S<sub>2y</sub> clusters, y = 5–8) was recently simulated with the ab initio SCF MO LCAO method [10]. The calculated data demonstrate clearly that Ni increases the adsorption ability of the surface centers, and the surface Ni atom itself is the most reactive site with respect to the hydrogen adsorption. This possibility has been mentioned by Prins and co-workers too [64].

We believe that generating the actual active centers in the HDS catalysts should involve the occluded hydrogen H<sub>o</sub>. After the H<sub>2</sub>S adsorption on the Co (Ni) atom, the d<sup>6</sup>-electronic state is stabilized. According to our experience, the Ni oxidation state in the Ni/MoS<sub>2</sub> catalyst increases with the oxidative addition of H<sub>2</sub> only in the presence of H<sub>2</sub>S [33]. As it was shown earlier, the occluded hydrogen is strongly bonded with

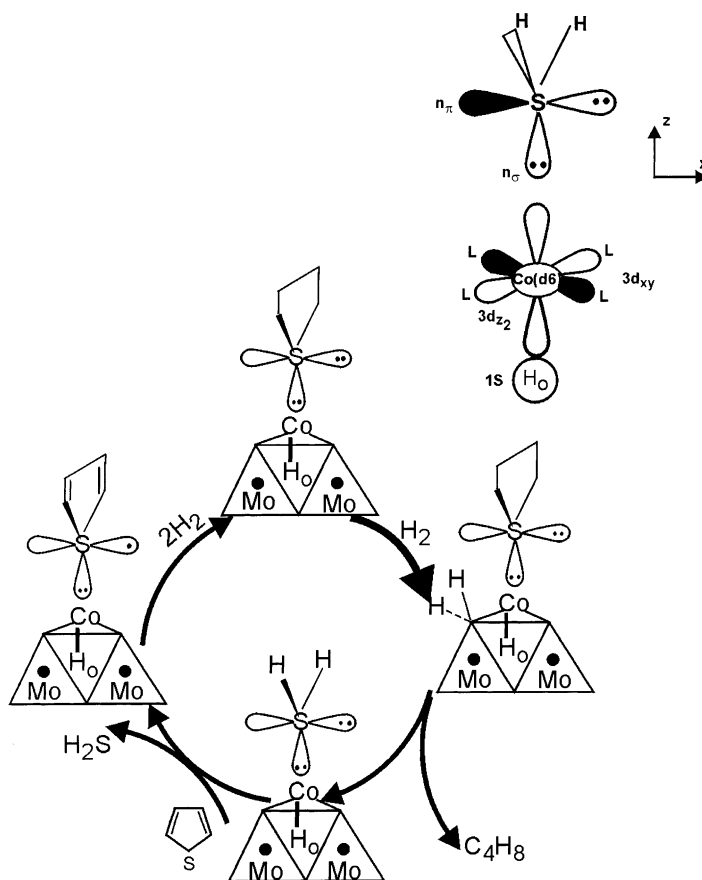


Fig. 7. A suggested scheme of the thiophene HDS catalytic cycle over Co/MoS<sub>2</sub>.

the active component matrix and can be removed at temperatures exceeding typical temperature of the catalytic reactions (300–400 °C). Therefore, the catalysts are stable working in the real conditions of hydrotreating for many years.

The HDS cycle for sulfide catalysts was proposed for many years [26,27]. Here, we consider this mechanism in more details taking into account the electronic structure of the active metal. We believe that the active center can not be “empty”, therefore, the initial and the final state of the active center should be a H<sub>2</sub>S adsorption complex (Fig. 7).

A thiophene molecule adsorbs on the active Co (d<sup>6</sup>) site thus replacing the H<sub>2</sub>S molecule. Indeed, the calculated values of  $E_{\text{ads}}$  (in the  $\eta^1$ -coordination which is shown in Fig. 7) evidence the H<sub>2</sub>S adsorption to be partially reversible under reaction conditions. Thus,

there should be the replacement of the adsorbed H<sub>2</sub>S molecule by thiophene. Thiophene hydrogenation destroys the  $\pi$ -system of aromatic ring, and an additional lone electron pair appears at the sulfur atom of tetrahydrothiophene (THT). Since THT is more basic than thiophene, it does not desorb into the gas phase [26,27]. Our preliminary ab initio calculations (at the Hartree–Fock level) of the adsorption energy in the series H<sub>2</sub>S (16.6 kcal/mol) < thiophene (18.4 kcal/mol) < THT (26.7 kcal/mol) support this assumption. Note that semi-empirical calculations give the same result [65].

After the tetrahydrothiophene molecule is stabilized on the active center, the electron density transfers from the sulfur atom of THT onto the catalyst, and localizes at the terminal S atoms on the side plane of MoS<sub>2</sub>. This creates a driving force for the dissociative

adsorption of dihydrogen. The activated hydrogen is transferred to the adsorbed THT molecule, and the process is terminated with the C–S bond scission and desorption of butene (butane) into the gas phase (Fig. 7). In another recent version of the HDS catalytic cycle for thiophene over the Co–Mo catalyst [66], the Co atom is also suggested to be an active site for the C–S bond hydrogenolysis. Regarding the calculated H<sub>2</sub>S and thiophene adsorption heats (16.6 and 18.4 kcal/mol, respectively) one may talk about the adsorption equilibrium between H<sub>2</sub>S and thiophene. Such equilibrium was experimentally shown to take place [67]. As the reaction temperature increases, the thiophene adsorption capacity becomes higher than that of H<sub>2</sub>S [68]. Relative adsorption constants for H<sub>2</sub>S and various thiophenes such as thiophene, benzothiophene and dibenzothiophene are considered in a study [69] according to which thiophenes adsorption constants are indeed higher than that of H<sub>2</sub>S.

## 9. Summary and conclusions

The data presented in this paper allow to draw the following conclusions.

- Ab initio calculations evidence that the oxidative addition of dihydrogen to the Ni(II) or Co(II) atoms is thermodynamically favorable and results in the stabilization of the Ni(IV) or Co(III) d<sup>6</sup>-electronic state in the composition of the active component of the sulfide HDS catalysts.
- The Ni(IV) or Co(III) atoms in the d<sup>6</sup>-electronic state behave as strong Lewis acids as evidenced with the IR stretching mode at 2233 cm<sup>-1</sup> of CO adsorbed on the active metal [70].
- Interaction of the thiophene molecule with the d<sup>6</sup> Ni(IV) or Co(III) cations occurs in the following manner: the lone electron pair n<sub>σ</sub> of the C<sub>4</sub>H<sub>4</sub>S molecule interacts efficiently with the vacant d<sub>σ</sub>-orbital of the Ni(IV) or Co(III) ion.
- Oxidative addition of hydrogen results in its occlusion into the MoS<sub>2</sub> matrix and stabilization in the center of a trigonal prism created by the sulfur atoms under the Ni or Co atom.
- The occluded hydrogen is strongly bound into the active component matrix and can be removed only at high temperatures (above 500 °C).

- The oxidative addition of dihydrogen may proceed easily when the electron-donor H<sub>2</sub>S molecule interacts effectively with the active metal (Ni, Co).
- There is an electronic interaction between coordinatively unsaturated S atoms in the edge plane of the MoS<sub>2</sub> macromolecule. The interacting atoms are capable for a dissociative adsorption of the dihydrogen molecule.

The idea on the feasibility of the oxidative addition of hydrogen is known to be a corner-stone in homogeneous catalysis to understand the mechanisms of many catalytic reactions involving activation of molecular hydrogen. Based on the profound identity of homogeneous, heterogeneous and enzymatic catalysis as a phenomenon with a common physico-chemical nature, we should expect the similar behavior of hydrogen in relation to the *same catalytically active metals* in the composition of solid and homogeneous catalysts. Therefore, the *purposeful* experiments should be initiated to prove this idea in heterogeneous catalysis. This task seems to be extremely difficult due to non-uniform composition of the surface active species in solid catalysts. So, the problem of synthesis of highly active and selective catalysts with a uniform composition of the active centers seems to be the main goal in developing the progress in this direction.

The sulfide catalysts of “metal complex origin” presented in this study may be considered as an example of such approach and the first step in understanding the unknown phenomenon in heterogeneous catalysis. No doubt that the oxidative addition of dihydrogen to metal atoms in heterogeneous catalysts is no less of dissemination as in homogeneous catalysis. We believe that new experimental evidence of this phenomenon will be found in the nearest future.

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