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Mechanism of the hydrogenolysis of thiophene on bimetallic sulphide catalysts

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ABSTRACT. **The structure of the sulphide bimetallic species (SBMS), which is the active component of hydrodesulphurisation catalysts, is examined. The main principles of the hydrogenolysis of thiophene on well-characterised sulphide catalysts have been analysed. A synchronous mechanism for the reaction of thiophene with hydrogen in the coordination sphere is considered and substantiated.**

The bibliography contains 143 references.

Contents

I. Introduction 175
II. General principles for the hydrogenolysis of thiophene on sulphide catalysts 175
III. Structure of the active component of hydrodesulphurisation catalysts 177
IV. Reaction mechanism of the hydrogenolysis of thiophene 181
V. Conclusion 185

I. Introduction

The hydrogenolysis of the C–S bond of organosulphur compounds is one of the key reactions occurring in the hydropurification of petroleum fractions. From the volume of sulphur being refined, hydropurification processes occupy a leading place and their output is growing more rapidly than those of other petroleum refining processes at the present time. The great practical value of the hydrorefining processes for petroleum fractions explains the enhanced interest of investigators in the study of the active component of hydropurification catalysts and their mechanism of action.[1–25]

To clarify the mechanism of a catalytic reaction in a heterogeneous system is more complex than in a homogeneous system. In spite of the many possibilities which the recently developed physical methods for investigating the surfaces of solid catalysts have created, the obtaining of detailed information on the structure of active centres is hindered by the non-uniform chemical composition of the surface compounds in real heterogeneous catalysts. Some of these compounds may be generally inactive in catalysis and surface formations which differ in structure may catalyse a given chemical conversion by various routes and mechanisms. The effect of the reaction medium on the catalyst is important. One type of surface compound may be transformed into another under the conditions of a catalytic reaction at high temperatures and pressures; this may cause a change in the mechanism of the reaction being studied. The problem also arises of synthesising highly active catalysts containing surface formations of one predominant type which are responsible for carrying out just the catalytic reaction in question. A further problem is the checking of the state of the catalyst surface under reaction conditions.

As is known, all hydrorefining processes for petroleum fractions are effected on one type of catalytic system, based on a composition of Mo (or W) with Ni (or Co) as sulphides. The results of numerous original studies on the synthesis and properties of sulphide hydrodesulphurisation (HDS) catalysts, the structure of their active component and the mechanism of the catalytic action have been correlated in several reviews and monographs.[1–25] In each of the reviews, reflecting some aspects of the action of HDS catalysts, the authors form and assert their own point of view on the mechanism of action bringing in further arguments from neighbouring areas of chemistry. Nevertheless these studies are based on two main hypotheses. 1) The active component is Mo(W) and Ni(Co) plays the role of promoter. 2) The HDS reaction takes place with the participation of anionic vacant sites on the $MoS_2(WS_2)$ by an oxidation–reduction mechanism.

An attempt is made in the present review to analyse critically these hypotheses and a new mechanism is proposed for the action of HDS catalysts. This is based on studies carried out in the Institute of Catalysis, Siberian Division of the Russian Academy of Sciences, where highly active sulphide HDS catalysts have been synthesised and characterised. The catalysts were made by attaching metal complexes of Mo, W, Ni and Co to the surface of various carriers (Al_2O_3, SiO_2, and the new carbon material 'Sibunit') with subsequent decomposition of the surface compounds by H_2S.

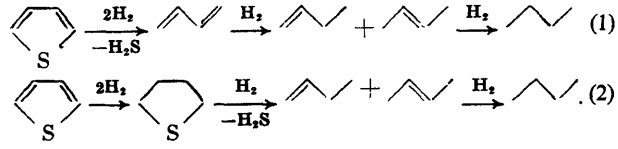
II. General principles for the hydrogenolysis of thiophene on sulphide catalysts

The hydrogenolysis reactions of thiophene and its derivatives are the slowest among the numerous reactions occurring during the hydrodesulphurisation of petroleum fractions, since the aromatic character of the thiophene ring hinders the elimination of sulphur from the molecule. Consequently the hydrogenolysis of thiophene and its derivatives is a generally accepted test for the properties of an HDS catalyst. From a scientific point of view the unsubstituted thiophene molecule is the most suitable for studying the mechanism of hydrogenolysis of the C–S bond, since substituents in the thiophene ring may have an appreciable effect on the coordination of the molecule to an active centre.

The hydropurification of crude petroleum is carried out at temperatures of 300–400 °C and H_2 pressures of 2–10 MPa.[1] The catalyst is in the sulphide state under the conditions of the

process. The inter-regeneration time of a catalyst is from several months to several years depending on the type of crude being refined and the specific consumption of a catalyst varies within the limits 15–60 g m^{-3} of crude.[26] These data indicate the high resistance of the catalysts to poisoning and becoming clogged with coke and the high thermal stability of the active component under process conditions.

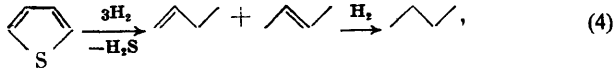
At the present time predominantly two possible routes for converting thiophene on sulphide catalysts are considered in the literature.[16]



In these cases the intermediate products are butadiene and tetrahydrothiophene (THT) respectively which are desorbed from the catalyst surface and may be detected in the gas phase. The possibility of the reaction proceeding by the following scheme may be considered as a variant of scheme (2).

$$T \rightarrow THT \rightarrow C_4H_6 + H_2S \rightarrow \text{products}, \quad (3)$$

where T is thiophene.[6] However a third route exists for the hydrogenolysis of thiophene,[27]



in which saturation of the thiophene ring and hydrogenolysis of the C–S bonds are effected at one active centre without loss of intermediates to the gas phase. This situation is effected on mono- and bimetallic sulphide catalysts both in bulk[28] and attached by various methods to SiO_2,[29] Al_2O_3 [30] and the carbon Sibunit carrier.[31] Catalysts are treated in H_2S at 400 °C before use to provide a steady level for their activity.[27–31] It was shown by special experiments[32] that the reaction route is not the consequence of the specific conditions of carrying out the process. The absence of butadiene and THT as intermediates in the hydrogenolysis of thiophene has also been recorded in other studies (see for example[33,34]), where the stationary activity of the catalysts was studied. We will return to the problem of possible routes for the conversion of thiophene after considering the reaction mechanism.

As already mentioned it is impossible to establish the mechanism of action of solid catalysts without knowing the structure of the active component. Traditional methods of preparing HDS catalysts are based on impregnating a preformed carrier with solutions of salts of the appropriate metals with subsequent drying, calcining and sulphurisation. This method does not allow a purpose-directed fixing of the composition of the active component or its immediate precursor.[35] The main reason for this is seemingly the complexity of the physicochemical conversions of the transition metals applied, including the processes of mass transfer and high temperature chemical interactions of the solid–solid type which are difficult to control.

The approach developed by Ermakov and collaborators[36,37] proved to be extremely productive when preparing catalysts with a fairly uniform content of active compounds on the surface. This comprises attachment of metal complexes of definite composition to a carrier surface and subsequently decomposing them under controlled conditions. This approach was also used for preparing highly dispersed sulphide catalysts.[29,30,38,39]

Catalysts are prepared in several stages. Initially organometallic or complex compounds of Mo or W are attached to the carrier (SiO_2 [29,38,39] or γ-Al_2O_3 [30]) and then, after appropriate treatment, Ni or Co are also applied to the Mo- or W-containing carrier in the form of organometallic or complex compounds. In several cases[30] the application of Ni(Co) was effected under conditions causing their adsorption to the Mo surface compounds. After drying, the catalysts were sulphurised in H_2S at 400 °C to provide a stationary level for their activity in the thiophene hydrogenolysis reaction.

Standard catalysts, prepared by the traditional impregnation method (ST), were studied in addition to the catalysts of metal complex (MC) origin. Among the former the greatest activity was possessed by catalysts obtained by a single impregnation (depending on the water content) of the carrier with an aqueous solution of the salts of the two metals with subsequent drying under an IR lamp, calcining in air at 500 °C and sulphurisation in H_2S at 400 °C. However the activity of standard catalysts prepared under optimum conditions was always less than the activity of samples of complex metal origin.[35]

Table 1. Specific (SCA) and atomic (ACA) activity of bimetallic sulphide catalysts in the hydrogenolysis of thiophene at 300 °C and the binding energy (E_b) of electrons at the Ni $2p_{3/2}$ level.[27–31,38–41]

Composition of and method of preparing catalysts *	SCA, mole $C_4H_4S \times 10^4$ / g.at (Ni+M).s	ACA, mole $C_4H_4S \times 10^3$ / g.at Ni.s	E_b** Ni $2p_{3/2}$, eV
0.18Ni/WS_2 (S_s = 10 m^2 g^{-1})	8.3 ***	28	853.8
0.60Ni/WS_2 (S_s = 39 m^2 g^{-1})	6.7 ***	25	854.0
(0.5Ni; 3.2W)/SiO_2 (MC)	156	48	854.0
(1.0Ni; 6.4W)/SiO_2 (ST)	50	15	–
(1.2Ni; 8.0W)/Al_2O_3 (ST)	48	16	–
(0.8Ni; 4.2W)/Sibunit (TC)	110	30	853.9
0.3Ni/MoS_2 (S_s = 9.0 m^2 g^{-1})	2.3 ***	4	853.9
(1.2Ni; 8.0Mo)/SiO_2 (MC)	89	16	853.9
(0.8Ni; 2.3Mo)/SiO_2 (ST)	30	8	–
(1.5Ni; 7.5Mo)/Al_2O_3 (MC)	103	42	854.2
(1.5Ni; 7.5Mo)/Al_2O_3 (ST)	21	9	854.0
(0.6Ni; 4.0Mo)/Sibunit (TC)	116	59	854.0

*The numbers before an element denote the content of the element in the catalyst, wt.%.

**E_b Ni $2p_{3/2}$ in α-NiS was 853.0 eV, and in $(NH_4)_2[Ni(WS_4)_2]$ was 853.8 eV.[38–41]

***Here SCA is in mole C_4H_4S m^{-2} s^{-1} × 10^8.

The specific activity of bimetallic sulphide MC catalysts applied to SiO_2 and Al_2O_3 was significantly greater than that of ST catalysts of closely similar composition (Table 1). In all cases the greatest

synergistic effect was observed at an atomic ratio Ni(Co):Mo(W) = 1:2 which corresponds with the majority of the known data.[8–14,21] The activity was reduced in the series (Ni, W) > (Ni, Mo) > (Co, Mo) > (Co, W).

Samples of similar chemical composition applied onto SiO_2 and Al_2O_3 by similar methods have approximately the same specific catalytic activity (SCA), however the SCA of catalysts applied to Sibunit is significantly greater. Possible reasons for this phenomenon will be examined in the following section.

The most characteristic feature of the reaction on all the bimetallic catalysts studied is the reduction in activation energy from 117 ± 8 kJ mol^{-1} in the temperature range 225–300 °C to 59 ± 8 kJ mol^{-1} in the range 300–400 °C (Fig. 1). Such a reduction in E_a is not a consequence of transition of the reaction into the diffusion region since it is characteristic of all catalysts independent of their pore structure and grain size, including the solid porous catalysts Ni/WS_2, Ni/MoS_2 and Co/MoS_2 which possess low specific activity.[29] Seemingly the reason must be sought in the change in the limiting stage of the reaction.

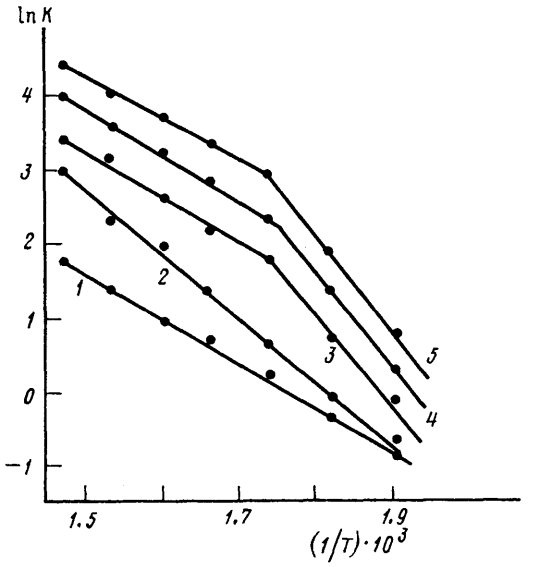


Figure 1. Temperature dependence of the reaction rate for the hydrogenolysis of thiophene on sulphide catalysts: *1*, Ni/Al_2O_3; *2*, Mo/Al_2O_3; *3*, Ni/MoS_2; *4*, $(Co-Mo)/Al_2O_3$; *5*, $(Ni-Mo)/Al_2O_3$.[29,30]

The products of the hydrogenolysis of thiophene on both mono- and bimetallic sulphide catalysts, prepared by various methods and on different carriers, contain only butene and butane in addition to H_2S.[27–31] Tetrahydrothiophene and butadiene are not present in the reaction products at the stationary level of activity of the catalysts. Trace quantities of butadiene were detected only on the most active (Ni–W) catalysts at a temperature of 400 °C and a degree of conversion of thiophene of 100%. The absence of possible intermediates from the reaction products is not a consequence of carrying it out with a large excess of hydrogen, since it was shown by special experiments[32] that a fairly high yield of THT may be obtained under the very same conditions on the very same Ni/SiO_2 and Mo/SiO_2 catalysts if, after sulphurisation, the catalysts are first reduced in H_2 at 400 °C. Significant quantities of butadiene (together with THT) were obtained under the same conditions on reduced zeolite NiY and MoY catalysts.[32]

The same principles for changing their activity in the hydrogenolysis of thiophene are characteristic of the sulphide catalysts (Ni, W), (Ni, Mo), (Co, Mo), and to a lesser extent (Co, W), applied by various methods onto Al_2O_3, SiO_2 and Sibunit. This indicates that the nature of the active component does not depend on the carrier type and method of preparation which affects only the level of activity of the catalysts. This inference does not pretend to be original, analysis of the vast scientific data on this problem leads readily to an analogous conclusion.

III. Structure of the active component of hydrodesulphurisation catalysts

The emergence at the beginning of the seventies of new methods of investigating the surface of a solid catalyst permitted an intensive study of the structure of the active component of HDS catalysts. According to the current classification,[20] 12 different models of the structure of the active component have appeared in the literature as ideas on the mechanism of action of the HDS catalysts have developed. The "Co–Mo–S phase" model is seemingly the most widespread[17,19,42–46] and was initially based on the results of an investigation of catalysts by Mössbauer emission spectroscopy and was then confirmed by the EXAFS method.

According to the "Co–Mo–S phase" model the active component is crystallised in the structural type of MoS_2, on a side face of a single patch of which Co atoms are localised. Other authors have subsequently arrived at a similar conclusion.[47–51] Though the similarity of the "Co–Mo–S phase" and MoS_2 structures is not in doubt there is no single opinion regarding the place of localisation of Co.

Substantially similar results on the structure of the active component of HDS catalysts were obtained in the Institute of Catalysis when studying the properties of highly active catalysts with a fairly uniform composition of surface compounds. A model for the structure of the active component was developed on the basis of the data obtained and was given the name sulphide bimetallic species (SBMS). The characteristic traits of this model will be examined.

1. Morphology of the surface of applied sulphide catalysts

The extended development of high resolution transmission electron microscopy (HRTEM) has enabled the limit of resolving ability of the electron microscope to be reached.[52] This method is used widely for studying the surface of applied catalysts containing ultradisperse particles of size less then 10 Å. On investigating HDS sulphide catalysts by the HRTEM method different authors obtained good agreement between their results.[31,53–58] When using various carriers (Al_2O_3, SiO_2, Sibunit, carbon) to obtain the catalysts, structures morphologically of a single type were detected on their surface irrespective of the method of preparation, the particle surface structure being characteristic of bulk MoS_2 and WS_2. The linear dimensions of the particles may vary within wide limits depending on the type of carrier and the method of preparing the catalyst. In the most disperse catalysts particles of size no greater then 20–25 Å

predominate,[56] but both finer (less than 10 Å) and more coarse (40–50 Å) particles may also be found on the surface.

In the majority of cases the active component is represented as single patches of $MoS_2(WS_2)$ the stabilisation of which is effected by abutting either the basal surface or the side face of the carrier. Well regulated structures which might be ascribed to Ni or Co sulphides were not detected in highly active catalysts. The reasons for the stabilisation of the highly disperse particles on the carrier surface will be examined.

Table 2. Structural characteristics of the carriers used for preparing sulphide HDS catalysts.[31,59,60]

Carrier	SiO_2	Sibunit	γ-Al_2O_3 *
Structure	Amorphous, chains of SiO_4 tetrahedra	Amorphous, flaky hexagonal	Cubic densely packed
Crystalline analogue	Tridymite, crystabolite	Graphite	Spinel $MgAl_2O_4$
Interatomic distances, Å	Si(1)–O(1)=1.6; Si(1)–Si(2)= =O(1)–O(2)=3.2; O(1)–O(1)=2.7; Si(1)–O(2)=4.0	d_{002}=3.356 C–C=1.42	Al_O–Al_O=O–O=2.79 Al_O–O=1.98; Al_T–O=1.71; Al_T–Al_T=3.42; Al_T–Al_O=3.29; O–O=3.95, 4.83

*Al_O and Al_T are aluminium atoms in spinel which occupy octahedral and tetrahedral positions respectively.

Table 3. Structural characteristics of Mo, W and Ni sulphides.[61]

Sulphide	MoS_2	WS_2	NiS
Structure	Flaky hexagonal	Flaky hexagonal	Very dense hexagonal
Structural type	Molybdenite MoS_2	Molybdenite MoS_2	Arsenide NiAs
Unit cell parameters, Å	a=3.16; c=12.395	a=3.187; c=12.52	a=3.427; c=5.31
Interatomic distances, Å	Mo–Mo=S–S=3.16; Mo–S=2.35; S–S=2.96 (patch thickness)	W–W=S–S=3.187; W–S=2.48; S–S=3.33 (patch thickness)	Ni–Ni=S–S=2.65; Ni–S=2.38

The structural characteristics shown in Tables 2 and 3 for sulphides and carriers indicate the closeness of the structures of $MoS_2(WS_2)$ and Sibunit. They belong to the same space group and crystallise in laminated hexagonal structures, the interplanar distances in Sibunit are close to the thickness of a single patch of $MoS_2(WS_2)$. Such a close similarity of structural types and interatomic distances assumes a possible epitaxial interaction of both the basal plane and the side faces. This picture was also observed in the electron microscopic prints. Single patches of the active component are disposed along the edges of the carbon carrier repeating its profile.[31] Evidently the oriented accretion of the active component on the Sibunit surface provides a limiting dispersity for the catalysts even when preparing them by the impregnation method and, as a result, a high activity in the thiophene hydrogenolysis reaction (see Table 1).

A closely similar picture is observed in the case of sulphide catalysts applied to SiO_2 using metal-complex precursors. In amorphous SiO_2 the SiO_4 tetrahedra are joined to one another by the apices in continuous chains which, interlinking with one another, form predominantly 6-membered units.[60] The interatomic O–O distances in the space lattice formed in this way are close to the S–S distance in the $MoS_2(WS_2)$ structure. Consequently on decomposing the surface metal complex in an atmosphere of H_2S the structure of an $MoS_2(WS_2)$ packet may be formed without fission of the Si–O–M chemical bond formed at the stage of applying the metal complexes. In this case also an epitaxial reaction of carrier and active component is therefore possible.

A different picture is seen for catalysts applied to γ-Al_2O_3. In spite of the absence of a geometric correspondence between the carrier structure and the structure of $MoS_2(WS_2)$, it is nevertheless possible to obtain highly dispersed sulphide particles which are thermally very stable and do not cake under the conditions of the catalytic process. Evidently for stabilisation of the highly disperse state it is sufficient either to interact the basal planes of the active component with the surface by Van der Waals forces or to form a relatively small number of bonds of the Al–S–M type between the side face of the active component and the surface of the Al_2O_3.[56]

Comparison of the particle sizes of the active component on the surface of SiO_2 and Al_2O_3 in catalysts prepared by various methods enabled the following conclusions to be drawn. The mean particle size in catalysts obtained on SiO_2 by impregnation was significantly greater than in MC catalysts which, together with the non-uniform composition of the surface compounds, may be one of the reasons for their comparatively low activity. On the other hand, sulphide particles in ST and MC catalysts applied to Al_2O_3 have approximately the same size,[56] consequently the lower activity of the impregnated samples may be explained either by the non-uniform composition of the sulphide particles or by the possibility of forming surface compounds during preparation which are not catalytically active. Evidently the most favourable situation arises on applying the active phase to Sibunit when highly active catalysts are successfully obtained by simple methods. In this case the geometric similarity of the structures of the carrier and the active component provide extreme dispersity for the latter and the carbon nature of the carrier enables phases inactive in catalysis to be avoided.

2. The electronic state of metals forming the active component

One of the main methods of studying the electronic state of metals in applied catalysts is X-ray photoelectron (XP) spectroscopy. The investigation of inorganic and coordination compounds of transition metals showed that the binding energy E_b of electrons in the inner levels of the central atom is a complex function of the oxidation level of the metal and the structure of its first coordination sphere.[62]

A large number of papers (see for example[55,58,63–66]) has been devoted to the study of sulphide catalysts by XP spectrometry. Most frequently the electronic state of Mo(W) in bimetal catalysts corresponds to their state in bulk $MoS_2(WS_2)$. The state of Co(Ni)

has not been assessed so unequivocally. The fact is that after sulphurisation of the impregnated catalysts the lines for Ni 2*p* and Co 2*p* in the XP spectra were markedly broadened, which is most probably linked with the presence of a certain quantity of Ni(Co) ions in the oxygen environment.[55,58,63,64,66] Consequently no changes of E_b were detected, compared to binary sulphide catalysts, for Ni $2p_{3/2}$ and Co $2p_{3/2}$ in bimetallic sulphide catalysts. At the same time a significant increase in E_b was noted for electrons of these levels in some studies,[31,40,64,65] while lines for Ni 2*p* and Co 2*p* in the spectra of MC catalysts were fairly sharp with a symmetrical maximum (Fig. 2), which indicates a similar environment for Co and Ni. The presence of an additional peak in the spectra of impregnated catalysts at a larger E_b shows that a certain quantity of Ni(Co) ions are in an oxygen environment.

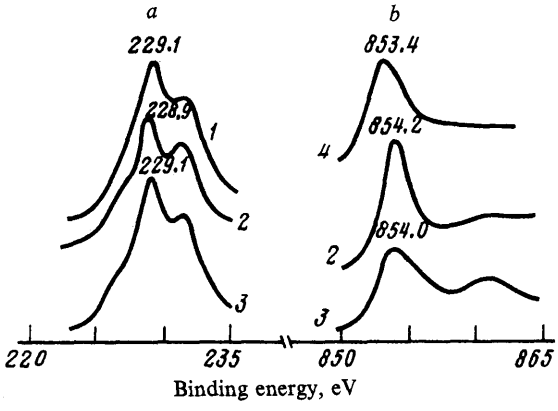


Figure 2. Profile of the *a*, Mo 3*d* and *b*, Ni 2*p* lines in the XP spectra of sulphide catalysts;[41] *1*, 4.5 Mo/Al_2O_3 (CM); *2*, (1.5 Ni, 4.5 Mo)/Al_2O_3 (CM); *3*, (1.2 Ni, 6.0 Mo)/Al_2O_3 (TC); *4*, 1.7 Ni/Al_2O_3 (CM).

The significant increase in E_b for Ni 2*p* and Co 2*p* in bimetallic catalysts in comparison with solid binary and applied sulphides (Table 1) was interpreted by us as a reduction in electron density on the Ni or Co atoms as a result of forming a new chemical compound, a SBMS, in which the Ni(Co) atoms are localised in the side face of $MoS_2(WS_2)$.[27,31,40] From the principles governing the change in E_b it is possible to assign a formal charge of +4 to this Ni(Co) atom. Closely similar values of E_b for Ni $2p_{3/2}$ are obtained for the $[Ni(WS_4)_2]^{2-}$ anion,[40,65] in which the Ni is in the centre of a square plane of S atoms.

3. Structure of dispersed particles of $MoS_2(WS_2)$ and the principle of the electrical neutrality of the molecule

As already mentioned above, the necessary structural unit on which the hydrogenolysis of thiophene can occur is a single patch of $MoS_2(WS_2)$ the linear size of which may vary from a few to several tens of angstroms. We now examine the structure of these highly disperse particles form the viewpoint of the principle of the electrical neutrality of the molecule. In the $(MoS_2)_x$ macromolecule all the valence bonds must be saturated when preserving the MoS_2 stoichiometry without changing the level of oxidation of Mo^{4+} and S^{2-}. In other words, in a macromolecule of any size the quantity of positive charges on the molybdenum atoms must be equal to the quantity of negative charges on the sulphur atoms. The excess (+) or (–) charges arising as a result of breaking valence bonds on the side face of a MoS_2 packet must be compensated by a corresponding quantity of charges opposite in sign. The problem of compensating the excess (–) charge on the terminal sulphur atoms was examined for the first time in 1980.[13]

The minimum structural unit determining the structure of a single MoS_2 patch is a trigonal prism made up of six S atoms in the centre of which is a Mo atom (Fig. 3). The formal excess charge of this cluster is 8 e^-, i.e. its chemical formula may be represented as $[MoS_6]^{2-}$. The macromolecule $(MoS_2)_x$ is formed by joining individual prisms along an edge, consequently a 'sandwich' is formed on joining three prisms, represented in projection from above as a regular hexagon. On the side face $(30\bar{3}0)$ of this hexagon there are two Mo atoms ($m = 2$) and on the $(0\bar{3}30)$ face one Mo atom ($n = m - 1 = 1$).

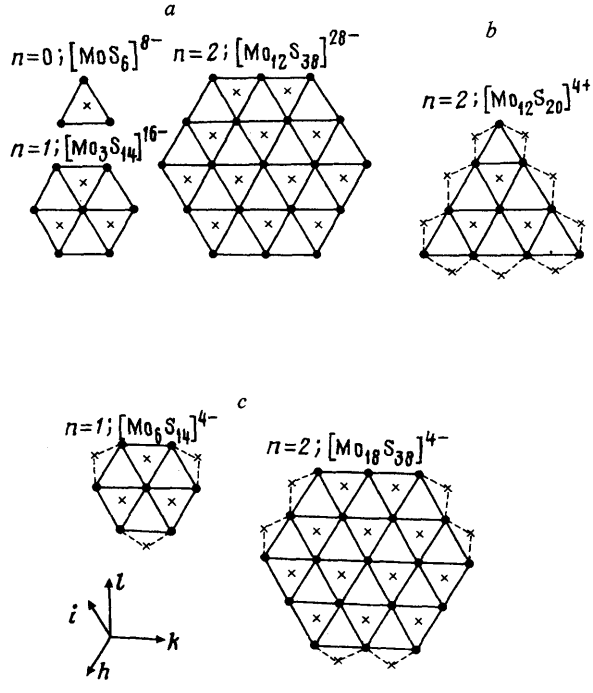


Figure 3. Formation of electrically neutral macromolecules of MoS_2 on putting into effect variants 1 (*a*), 2 (*b*) and 3 (*c*) (see text).

In the hexagon formed by three prisms there are 3 Mo and 14 S atoms which makes an excess charge of 16 e^-, i.e. the formula of the cluster is $[Mo_3S_{14}]^{16-}$. On increasing the length of the rib by one more Mo atom ($m = 3$, $n = 2$) the formula for the cluster will be

$[Mo_{12}S_{38}]^{28-}$. It is easy to show that in the general case a regular hexagon is described by the formula $[Mo_{(3n^2)}S_{2(3n^2+3n+1)}]^{(12n+4)-}$. With an increase in length of the rib the ratio of the sum of (–) charges on the S atoms to the sum of (+) charges on the Mo atoms in an infinitely large molecule $(MoS_2)_x$ will therefore be

$$\lim_{n\to\infty}\frac{4(3n^2+3n+1)}{12n^2}=1,$$

i.e. an infinitely large molecule is electrically neutral.

A significant excess of (–) charges will always exist in the case of a macromolecule of size $\leqslant 25$ Å ($n \leqslant 6$). An electrically neutral macromolecule may be formed by three different routes: 1) by adding protons to form S–H groups, 2) by removing excess S atoms with the formation of anionic vacant sites, 3) by adding additional Mo^{4+} atoms or other cations (Ni, Co, etc.).

We will examine these cases in more detail.

Variant 1. The adsorption of H_2 by bulk MoS_2 is well established experimentally and the presence of S–H groups has been confirmed spectroscopically.[67,68] The possibility of homolytic and heterolytic dissociation of dihydrogen on a MoS_2 surface has been shown by theoretical calculations.[69]

In the present case, $(12n + 4)$ protons are necessary to compensate the excess charge on the cluster the rib of which consists of n atoms of Mo which corresponds to the formula $H_{(12n+4)}Mo_{(3n^2)}S_{2(3n^2+3n+1)}$. This formula may be rewritten in the form $3n^2(MoS_2).2(3n + 1)H_2S$ from which it follows that the atomic ratio S:Mo is always greater than 2. Since this result contradicts numerous data according to which the ratio S:Mo < 2 and also the experimental data[67,68] on the quantity of H_2 adsorbed by MoS_2, it may be concluded that compensation of the (–) charge is probably not solely by addition of protons.

Variant 2. The possibility of removing peripheral S atoms with the formation of anionic vacant sites has been considered in many studies where the formation of adsorption centres and the activation of the reagents were examined (see, for example[70,71]). If the principle of the electrical neutrality of the macromolecule is followed then it is easy to show that to compensate for the (–) charge on a cluster the rib of which consists of n Mo atoms, it is necessary to remove all the S atoms on the side face $(10\bar{1}0)$ (Fig. 3, *b*). In this case the molecule is bordered by molybdenum atoms in the $(30\bar{3}0)$ plane and the quantity of S atoms remaining in the molecule is $(6n^2 - 4)$. Consequently the hexagon may be described by the formula $Mo_{(3n^2)}S_{(6n^2-4)}$, which in an infinitely large molecule

$\lim_{n\to\infty}\frac{6n^2-4}{3n^2}=2,$ corresponds to the formula MoS_2. A small excess of (+) charge is characteristic of clusters of a smaller size.

Variant 3. Extra cations, particularly Mo^{4+} may be added to the terminal S atoms on the $(10\bar{1}0)$ plane and occupy the regular positions of the MoS_2 lattice prescribed for Mo^{4+} ions during the growing process of the macromolecule (Fig. 3, *c*). In this case the formula of the macromolecule has the form $Mo_{(3n^2+3n)}S_{2(3n^2+3n+1)}$ which means that an infinitely large molecule is also described by the formula MoS_2. A small excess of (–) charges is observed in clusters of smaller size. Comparison of Figs. 3, *b* and 3, *c* show that variant 3 is a derivative of variant 2 with removal of angular Mo atoms and the corresponding quantity of S atoms.

The additional Mo^{4+} cations belonging to the side face $(30\bar{3}0)$ are coordinationally unsaturated. Following the principle of minimum free energy at the phase separation border, it may be proposed that the cations in question are able to shift from their regular positions towards the centre of the hexagon (Fig. 4), which may lead to the appearance of additional (+) charge on the peripheral $Mo^{(4+\delta)+}$ atoms. In our opinion this enables the small excess of (–) charge on small clusters to be compensated. It may also be proposed that these $Mo^{(4+\delta)+}$ cations are centres for adsorption and activation of donor molecules, i.e. they act as catalytically active centres.

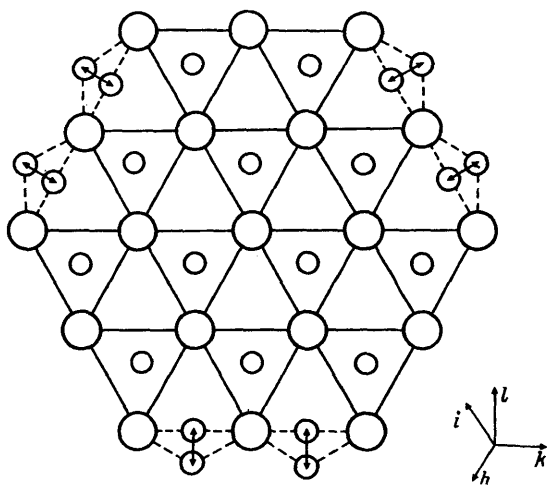


Figure 4. Displacement of cations from the regular positions of the lattice on the periphery of a MoS_2 patch.

In many respects a similar situation arises in the compensation of (–) charge on the terminal S atoms in the plane $(10\bar{1}0)$ after their coordination with Ni^{2+} or Co^{2+} cations. However since square-planar coordination[73–78] is characteristic for compounds of these metals with chelated sulphur-containing ligands then it is most probable that these cations occupy the centre of a square of S atoms in a plane $(10\bar{1}0)$ on the periphery of a $MoS_2(WS_2)$ patch (Fig. 4). With such coordination additional (+) charges on the Ni(Co) ions, corresponding to the formal oxidation level of 4+, are necessary to form electrically neutral fragments. A similar increase in charge was recorded by XP spectroscopy (see above). It is known[78] that reversible electron transfer reactions with the formation of stable products readily occur in square-planar complexes with S-containing ligands.

Evidently the compensation of the excess charge on the terminal S atoms by the addition to them of transition metal cations has a more general character. Thus after applying copper ions to a WS_2 surface a significant reduction was also detected in the electron density at the Cu atoms compared with the binary sulphide.[79] Even more, after applying Ni to the surface of both bulk and applied NbS_2 and ReS_2 (both these sulphides crystallise in the molybdenite

MoS_2 structure[80,81]) a reduction in the electron density on the Ni atoms compared with NiS was also recorded.[79] These observations serve as grounds for proposing that the coordinationally unsaturated electron-deficient atoms of Ni(Co) may act as centres for adsorption and activation of donor molecules.

4. The structure of the sulphide bimetallic species

In the previous section we came close to examining the structure of the active component of HDS catalysts known as the sulphide bimetallic species (SBMS).[27,72,82–86] The structural data forming the basis of this model were obtained by EXAFS [82] and by the X-ray method for the radial distribution of atoms (RDA).[60] According to this model the active component of the HDS catalyst is a uniform patch of $MoS_2(WS_2)$ on the side face $(10\bar{1}0)$ of which the Ni(Co) atoms are located (Fig. 5). In the SBMS the Mo(W) atoms are in the centre of trigonal prisms and are surrounded by six S atoms, the distances being Mo–S = 2.41 Å and W–S = 2.46 Å. The prisms are joined along an edge forming a 'sandwich' in which the distance Mo–Mo = 3.17 Å and W–W = 3.24 Å. All the values given for the interatomic distances are typical of bulk MoS_2 and WS_2.

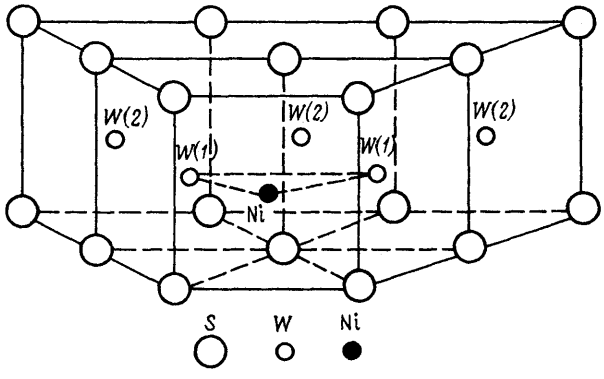


Figure 5. Stucture of the sulphide bimetallic species (SBMS), the active component of HDS catalysts.

When the Ni(Co) is located in the centre of a square of sulphur atoms in the plane $(10\bar{1}0)$, the distance Ni–S = 2.2 Å and Ni–W = 2.4 Å. Precisely the same values were found by EXAFS.[82] It must be emphasised that the distance Ni–S = 2.15–2.20 Å is typical for square-planar complexes with chelated S-containing ligands.[73–76] The short Ni–W distance = 2.4 Å suggests the formation of a direct metal–metal bond between the dissimilar atoms.

The closely similar values of the interatomic distances, particularly Co–S and Ni–S = 2.2 Å, were also found in other studies, however the Mo–Mo distance proved to be longer ~2.8 Å.[87,89] It was confirmed by XANES that the square-planar environment of the Ni atoms was transformed into trigonal-pyramidal after adsorption of a S-containing molecule.[88] It may be suggested that the increase in the Ni(Co)–Mo distance to 2.8 Å is explained by the fact that after adsorption of the donor molecule (H_2S in particular) onto Ni(Co) atoms forming part of the SBMS these atoms emerge from the plane $(10\bar{1}0)$ (Fig. 6). Such a situation is typical of pentacoordinated metal complexes. When the donor molecule occupies a pentacoordinate position in a square-planar complex a compound is formed in which the metal is in a square-pyramidal environment.[90]

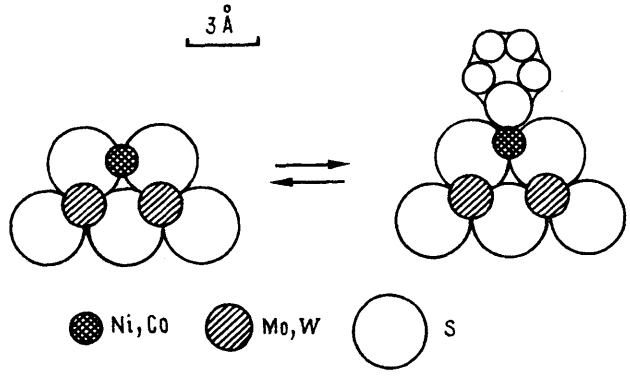


Figure 6. Adsorption of the thiophene molecule on SBMS.

IV. Reaction mechanism of the hydrogenolysis of thiophene

All the reaction mechanisms considered in the literature on the hydrogenolysis of the C–S bond are based on two main hypotheses.

1. The reaction is considered as a multistage oxidation–reduction process with the participation of anionic vacant sites of MoS_2 or Co–Mo–S phases.[8–19] Apparently one of the first mentions of the participation of anionic vacant sites of sulphide catalysts in the catalytic cycle appeared in 1969.[91] It may be suggested that this hypothesis arose from ideas on reaction mechanisms on oxide catalysts. Up to the present, fairly persuasive confirmation has been obtained of the participation of surface oxygen atoms of solid catalysts in the catalytic cycle.[92,93]

2. The active component of the catalyst is considered to be MoS_2, on the anionic vacant sites of which adsorption and activation of the S-containing molecule occurs. The Ni(Co) atoms are assigned the role of promoters. Various authors assess the role of promoters in a different way leading either to activation of hydrogen,[20] or to increase the number of anionic vacant sites,[22] or to the creation of qualitatively new types of vacant sites,[17,19,22] etc. The hypothesis on the distribution of roles between the active components and promoter is based, seemingly, on the following considerations. In the first place it is well known that addition of even small quantities of Ni(Co) to Mo(W) in the sulphide form leads to a sudden non-additive growth in activity, while addition of small quantities of Mo(W) to Ni(Co) sulphide causes only an insignificant increase in it. Secondly, modern methods, particularly electron microscopy, have shown the presence of $MoS_2(WS_2)$ particles in the catalysts (see part 1 of section III), while structures typical of Ni(Co) sulphides have not been detected.

The participation of anionic vacant sites in the catalytic cycle was also assumed on the basis of theoretical calculations on the reaction of thiophene with an MoS_2 surface.[94,95] The possibility of coordinating thiophene to an anionic vacant site through the S atom (η^1-coordination) and through the plane of the ring of the molecule (η^5-coordination) was examined in this way.

Table 4. Comparison of the amount of sulphur removed on TPR, the rate of exchange with $H_2{}^{35}S$ and the activity of sulphide catalysts in the hydrogenolysis of thiophene.[27,107]

Catalyst	Amount of sulphur removed on TPR in the range 25–500 °C, as % S content of the initial catalyst	Initial rate of isotopic hetero-exchange with $H_2^{35}S$ at 300 °C, g. at S/[g.at (Ni+M).s] × 10^3	Activity on thiophene hydrogenolysis at 300 °C, mole C_4H_4S/[g.at(Ni+M).s] × 10^4
Ni/SiO_2	100	–	2
Mo/SiO_2	35	42	5
$(Ni, Mo)/SiO_2$	41	36	60
W/SiO_2	26	–	3
$(Ni, W)/SiO_2$	31	25	123

However both of these suggestions are no more than hypotheses since there is no direct experimental confirmation and the indirect correlations are extremely inconsistent. We shall examine these hypotheses in more detail.

1. Participation of anionic vacant sites of $MoS_2(WS_2)$ in the catalytic cycle

Anionic vacant sites on the surface of sulphide particles may arise by the reaction of surface sulphur atoms with H_2 at elevated temperature and their removal as H_2S. The number of anionic vacant sites may be determined from the quantity of H_2S evolved in a temperature-programmed reduction (TPR) of the sulphide catalyst,[96,97] and also from the quantity of donor molecules adsorbed on the surface of sulphide catalysts after reducing them in H_2 at a particular temperature.[98–103] Both these procedures were used to construct correlation relationships. In some cases a correlation with catalyst activity in the hydrogenolysis of the C–S bond was detected[96–100] and in others it was absent or was not clearly displayed.[101–103]

To assess the mobility of oxygen in oxide catalysts and to study its role in catalysis, the method of hetero-exchange with oxygen in the gas phase has been widely used.[92,93] In the case of sulphide catalysts H_2S, labelled with the radioactive ^{35}S isotope, may serve as the appropriate test molecule.[104–106]

Correlations between catalytic activity and the mobility of surface S atoms were not detected by TPR or by $H_2{}^{35}S$ exchange methods on highly active sulphide catalysts.[27,107] After the addition of Ni to Mo(W) catalyst the rate of $H_2{}^{35}S$ exchange with the surface was reduced but the quantity of sulphur removed in the TPR process was practically unchanged and the activity of the catalyst was increased many times (Table 4).

A calculation of the enthalpy of the reaction of H_2 and sulphur atoms belonging to different faces of a single $MoS_2(WS_2)$ patch has been made by the interacting bond (IAB) method.[72] It turned out that to remove sulphur atoms from the basal plane $(000\bar{1})$ and from the side face $(0\bar{1}10)$ it was necessary to expend 335–398 and 92 kJ mol^{-1} respectively while the reaction of H_2 with S atoms in the plane $(10\bar{1}0)$ was characterised by a negative value of ΔH = 21–42 kJ mol^{-1}. This indicates that the removal of peripheral S atoms from plane $(10\bar{1}0)$ is energetically advantageous and consequently may occur even on forming a single $MoS_2(WS_2)$ patch.

As a result of forming an electrically neutral macromolecule (Fig. 3, *b*, *c*) the sulphur atoms which may be removed as H_2S are found in plane $(0\bar{1}10)$ and are coordinated with two Mo(W) atoms, i.e. for their removal ~92 kJ mol^{-1} is required. However the addition of S atoms to the vacant site formed is accompanied by a significant energy advantage. The enthalpy of this reaction is ΔH = –239 kJ mol^{-1}.[72] This indicates that under the conditions of the catalytic reaction the electrically neutral molecule must be thermodynamically stable since the reaction equilibrium is shifted strongly to the left.

$$S+H_2 \rightleftarrows \square+H_2S.$$

A similar situation also arises in the case of the bimetallic catalysts. Calculations within the framework of IAB show[72] that it is necessary to expend 50–63 kJ mol^{-1} to remove sulphur atoms coordinating Ni(Co) atoms in the SBMS, while their addition to the vacancies formed is accompanied by an energy advantage of ~209 kJ mol^{-1}. Consequently in this case also the electrically neutral SBMS is a thermodynamically stable unit.

An important conclusion emerges from comparison of the enthalpy of the addition of S and removal of S from sulphide catalysts of various composition.[72] Since, according to Temkin's rule,[108] the rate of the two-stage catalytic process is maximal if the Gibbs' energies of both stages are approximately the same, the structure-forming sulphur atoms, i.e. those atoms which form the structure of the electrically neutral SBMS, may not participate in the catalytic cycle. Only those S atoms which have just one chemical bond with a metal atom may be catalytically active. This rule is better satisfied by the coordination of sulphur to the Ni or Co atoms than to Mo or W.

Examination of the thermodynamics of forming vacant sites on the surface of an electrically neutral SBMS places doubt on the possibility of their participation in the catalytic cycle. The absence of a correlation between the catalytic activity and the mobility of the surface sulphur atoms is inconsistent with this hypothesis.

2. The role of Ni(Co) and Mo(W) atoms in the activation of reacting molecules

The reductive desulphurisation of thiophene became apparent more than half a century ago[109] when it was discovered that benzene or toluene may be completely purified from thiophene contamination with Raney nickel. Subsequently the method of reductive desulphurisation of thiophene compounds was widely used in preparative organic chemistry both to establish the structure of thiophene derivatives and also for the synthesis of various saturated systems.[110–114] Raney cobalt is less suitable for these purposes.

The reductive desulphurisation of thiophene and its derivatives occurs on Raney nickel under very mild conditions. As a rule it takes place at room or elevated temperature (60–80 °C) using fairly inert solvents such as diethyl ether, ethanol, toluene, etc.[109–114] A necessary condition for high yield is the presence of hydrogen dissolved in the Raney nickel which is formed in the process of leaching out the Ni–Al alloy and is retained for a long time in large quantities in the bulk of the Raney nickel.[115] Usually the reaction is carried out in the absence of hydrogen in the gas phase and with an excess of Raney nickel. The reaction takes place fairly smoothly. Sulphur from the substrate molecule is irreversibly adsorbed onto the surface, deactivating it. The olefinic bonds are reduced with the evolution of aliphatic molecules into the gas phase. This reaction must be considered to be stoichiometric rather than catalytic[110,111] since it is necessary to remove the bound sulphur to complete a catalytic cycle. Seemingly this is impossible to accomplish under the conditions of the reaction since Ni sulphides are only reduced at a higher temperature.

Numerous experimental data convincingly point to a radical mechanism for the hydrogenolysis of a C–S bond on Raney nickel.[110,112] Fission of the C–S bond occurs after adsorption of the S-containing molecule with the formation of firmly bound sulphur and free radicals. The latter are saturated by the dissolved hydrogen and when this is absent the saturation of the free valencies occurs by dimerisation or disproportionation.[110]

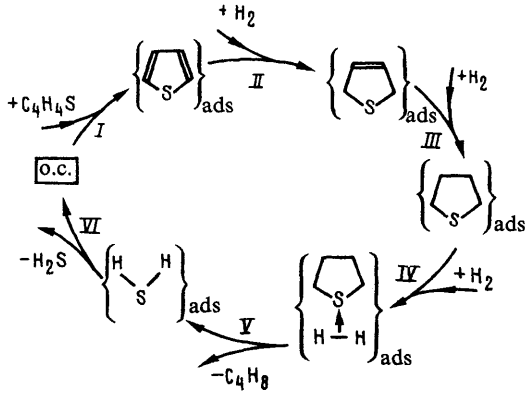
The desulphurisation reaction of dibenzothiophene (DBT) and its derivatives on Ni complexes, which also occurs under very mild conditions, is very representative.[116] The reaction of (2,2′-bipyridyl)-(1,5-cyclooctadiene)nickel(0) with DBT at ~60 °C is accompanied by the formation of only small quantities of diphenyl and its derivatives with nickel.[117] However if this complex of Ni(0) is first treated with $LiAlH_4$ in a molar ratio of 1:2 then the resulting complex will carry out the desulphurisation of DBT in quantitative yield.[116,118] These results indicate that nickel is extremely active in the fission of a C–S bond, however an excess of activated hydrogen is required to bring about the process.

A detailed study of the catalytic properties of Ni sulphides has shown[70] that they are inactive in H_2-D_2 exchange, in deuterium–hydrogen exchange reactions with olefins and in the hydrogenation of olefins at low temperatures. These catalysts begin to display activity only after reduction in H_2 at elevated temperatures. In addition the stoichiometric sulphides CoS, CoS_2, Co_9S_8 and Ni_3S_2 proved to be inactive in the hydrogenation of dienes.[119,120] However CoS in the absence of hydrogen accelerated the reaction of buta-1,3-diene with cyclohexa-1,3- and 1,4-dienes and also the disproportionation reaction of cyclohexadiene.[120] These data indicate the difficult activation of hydrogen on Ni and Co sulphides.

In contrast, MoS_2 is active in the hydrogenation of olefins and dienes at low temperature[118] and carries out the H_2-D_2 exchange reaction even at −40 °C.[121,122] Hydrogen is adsorbed in the dissociated form on MoS_2 and WS_2 with the formation of S–H groups.[67,68,123] From this it may be concluded that the activation of H_2 on $MoS_2(WS_2)$ occurs fairly readily.

The activation of hydrogen under mild conditions (25–75 °C, H_2 pressure 2 atm) is also effected on molybdenum complexes with S-containing ligands.[124–127] The resulting S–H groups readily hydrogenate olefinic and acetylenic hydrocarbons.[127]

On the other hand the heats of formation of MoS_2 (272 kJ mol^{-1}) and WS_2 (259 kJ mol^{-1}) are far greater than the heat of formation of NiS (71 kJ mol^{-1}).[128] Nickel sulphides readily lose sulphur in an atmosphere of H_2 and are reduced to the metal even at 300–400 °C while Mo and W disulphides are fairly stable at these temperatures.[27] In other words, the strength of the M–S bond in Mo or W sulphides is greater than in Ni sulphides.



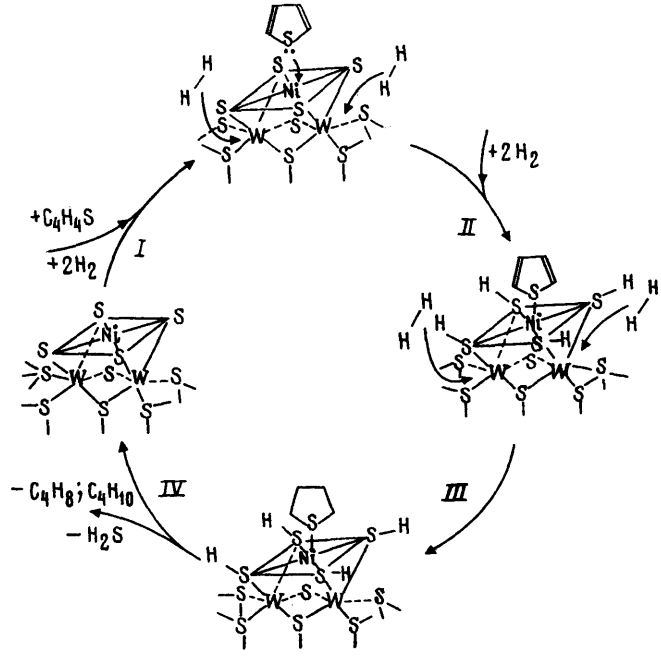
A catalytic cycle is shown for the hydrogenolysis of thiophene in six sequential stages, in each of which adsorption and activation of the reactants or desorption of the products occurs. The separation of the overall reaction into these stages is arbitrary since their number and sequence may be different. It is only important that the possible intermediates are strongly adsorbed on the catalyst and are not evolved into the gas phase during the entire catalytic cycle.[27,86] In spite of its arbitrary nature such a scheme for the conversion is convenient for examining the problem of the limiting stage of the reaction.

In the light of the arguments mentioned above one of the stages *II–IV*, in which activation of molecular hydrogen occurs, may be considered to be probably limiting for reaction on Ni(Co) sulphide catalysts. The stage for fission of the Ni–S(Co–S) bond and the desorption of H_2S into the gas phase (*VI*) seems to be rapid. On the other hand, stages *II–IV* are probably rapid on $MoS_2(WS_2)$ and the stage determining the rate of the whole process may, for example, be the removal of sulphur from the active centre (stage *VI*).

The clearly defined non-additive increase of the activity of bimetallic sulphide catalysts may be explained by the fact that those stages which determine the overall reaction rate on monometallic catalysts remain rapid. However for this it is necessary to assume that the adsorption of thiophene on Ni(Co) atoms occurs with the formation of a labile M–S bond and the ease of activation of H_2 on $MoS_2(WS_2)$ provides rapid hydrogenation of the thiophene ring. Then a different stage may become limiting, for example stage *V* in which fission of the C–S bond occurs.

3. Synchronous mechanism for the hydrogenolysis of thiophene in the coordination sphere of the SBMS

Analysis of the arguments mentioned above and the experimental data enable the following mechanism to be proposed for the hydrogenolysis of thiophene on a SBMS.



According to this mechanism the thiophene molecule is adsorbed on coordinationally unsaturated Ni(Co) atoms existing in a square-planar environment of S atoms. The deficiency of electron density on the Ni(Co) atoms enables coordination to them of an S atom, which in the thiophene molecule has an unshared electron pair. Simultaneously with the adsorption of thiophene on Ni(Co), activation of H_2 may occur in parallel and independently on Mo(W). The activated hydrogen may be passed on to the thiophene molecule, for example, via the S atoms coordinating the Ni(Co). However, other possible transfers of activated hydrogen are not excluded if the short metal–metal distance between the dissimilar atoms is taken into account, assuming the formation of a direct chemical bond. Seemingly the activation of hydrogen occurs continuously with its consumption in the hydrogenation of the thiophene ring. We propose that stages *I–III* for the activation of hydrogen and thiophene occur rapidly and stage *IV*, the fission of the C–S bond may be limiting after which the reaction products (H_2S, butenes, butane) are rapidly desorbed into the gas phase. The high rate for the process is provided by the synchronous interaction of reactants in the coordination sphere of the SBMS. A significant portion of the energy consumption on activating the reactants is compensated by the heat of adsorption and the hydrogenation energy of the thiophene ring, indicated by the low value of the activation energy $E_a = (59 \pm 8)$ kJ mol^{-1} (see Fig. 1).

Direct experimental confirmation of the proposed reaction mechanism has been obtained recently. It was shown by EXAFS *in situ* that the chemosorption of the selenophene molecule (the structural analogue of thiophene) on sulphide catalysts (Ni, Mo)/Al_2O_3 (MC) occurs only on the Ni and not the Mo atoms forming part of the SBMS.[129] Similar conclusions were reached previously.[88]

In order to answer the question of why thiophene is adsorbed by SBMS and H_2S is desorbed but the possible intermediate THF is not desorbed, the heats of adsorption of these molecules on SBMS of various composition were calculated within the framework of the IAB method.[130] The calculated heat of adsorption of H_2S was 48–52, of thiophene 88–94 and of THT 146–155 kJ mol^{-1}. The low value of the heat of adsorption of H_2S indicates the reversible nature of its adsorption under the reaction conditions and the possibility of displacing adsorbed hydrogen sulphide by thiophene. The significantly greater heat of adsorption of THT indicates that it is adsorbed practically irreversibly and the only possible variant of the catalytic cycle is hydrogenolysis of a C–S bond with desorption of hydrogen sulphide and hydrocarbons into the gas phase. Seemingly the main reason for the strength of the binding of THT to the active centre is the basicity of this S atom which is higher than that of thiophene and is caused by a reduction in the π-resonance energy on hydrogenating the aromatic thiophene molecule.

An additional argument in favour of the axial coordination of thiophene to the Ni(Co) atom (see Fig. 6) may be the existence of well-studied square-planar metal complexes with chelated macroligands.[131] The ability of square-planar complexes to undergo a reversible electron transfer reaction with the formation of stable products and the high electron-accepting ability of these complexes in relation to an organic donor have been well studied.[78,132]

The coordination of the thiophene molecule to a Ni(Co) atom in an SBMS is accompanied by a change in its coordination state. The adsorbed molecule adds on to the environment of the Ni(Co) to make a square pyramid which seemingly leads to a displacement of the Ni(Co) atoms from the centre of the square formed by the S atoms in the $(10\bar{1}0)$ plane of the SBMS (see Fig. 6). Such a displacement of atoms is very characteristic of square-planar metal complexes when they are transformed into pentacoordinated complexes after coordination of the donor ligands.[90] It is evident that the shift of Ni(Co) atoms is accompanied by a lengthening of the Ni(Co)–Mo distance. This effect has been observed in other studies.[87–89]

4. Other routes for converting thiophene

The synchronous mechanism for the hydrogenolysis of thiophene on SBMC enables the absence of the possible intermediates THT and butadiene from the gas phase to be explained. However they were recorded nevertheless in several cases when carrying out the reaction on one type of catalytic system. One of the most probable explanations for this discrepancy is the presence on the catalyst surface of other active centres, different from the SBMS, which may catalyse this reaction by a different route.

For some time past much attention has been paid to the study of the hydrogenolysis of the C–S bond on various faces of Mo, W and Ni single crystals.[24,25] The first stage of the hydrogenolysis of thiophene on Mo face (100) is fission of the C–S bond with evolution of butadiene into the gas phase.[133] The limiting stage of the reaction is the hydrogenation of sulphur adsorbed on the surface of the monocrystal.[134] At the same time propylene is the main product of THT hydrogenolysis and therefore THT cannot be an intermediate in the hydrogenolysis of thiophene.[133]

The desulphurisation of thiophene proceeds in a different way on a W surface (211).[135] The main product of the temperature-programmed desorption is propylene which indicates fission of a C–C bond at the α-carbon atom of the thiophene molecule. On the other hand with a Ni (111) surface, hydrocarbons C_{5+} are desorbed which implies dimerisation and possibly disproportionation of the reaction products.[136] However since the reaction took place in the absence of hydrogen,[135,136] one should speak of cracking and not hydrogenolysis in these cases.

Nevertheless the data on the reaction of thiophene with the surface of single crystals shows that the first stage of the process is fission of a C–S bond with subsequent saturation of the free valencies of radicals by reaction with H_2 or by recombination.

One way of clarifying the action mechanisms of solid catalysts is the study of the coordination of substrate molecules to the metal complex stabilised with different ligands. Although a large number of stable metal complexes of thiophene with various transition metals exist,[23,25] only a few of them include metals forming part of HDS catalysts.[137,138] A thiophene molecule coordinated to a metal through the S atom may be readily replaced by a weak ligand.

The preparation of THT by the catalytic hydrogenation of thiophene is not a simple problem. From a preparative point of view the ionic and electrochemical hydrogenation of thiophene are the most acceptable methods.[139] The hydrogenation of thiophene with molecular hydrogen is complicated by the rapid poisoning of the catalysts and by side reactions of hydrogenolysis of the C–S bond. Seemingly the most effective catalysts are based on noble metals and also rhenium sulphide.[140]

The appearance of THT among the hydrogenolysis products of thiophene on sulphide HDS catalysts may be linked with the formation of qualitatively new active centres. As has been shown[27,32,86] at a given level of activity of mono- and bimetallic sulphide catalysts based on Ni, Co, Mo and W prepared by various methods using various carriers, the hydrogenolysis of thiophene leads to the evolution only of H_2S, butenes and butane. The appearance of significant quantities of THT in the gas phase was observed under

the same conditions and on the same monometallic sulphide catalysts if, before carrying out the reaction, the catalysts are reduced in H_2 at 400 °C after sulphurisation in H_2S.[32] It was concluded from this that the responsible metal ions were in a low oxidation state after the reaction of hydrogenation of thiophene to THT. They may arise as a result of reduction of the catalyst surface either on carrying out the reaction in a non-stationary mode (for example, using pulse equipment in a H_2 stream), or with a deficient sulphur content in the raw material (for reoxidation of the catalyst surface), or in the presence in the catalyst of active centres different from the active centres of the HDS sulphide catalysts and not forming sulphides under the reaction conditions. It is more probable that the thiophene molecule is coordinated to that type of active centre not through the sulphur atom but by π-binding of the ring of the molecule.

V. Conclusion

Analysis of the principles for carrying out the hydrogenolysis of thiophene on highly active sulphide catalysts has enabled a new reaction mechanism to be proposed. The characteristic features of the proposed mechanism are as follows.

1. The hydrogenolysis of thiophene occurs within the coordination sphere of a sulphide bimetallic species without the participation of structure-forming sulphur atoms in the catalysis.

2. The adsorption and activation of the thiophene molecule is effected on Ni (or Co) atoms in the composition of the SBMS and the activation of H_2 occurs with the participation of Mo (or W) atoms.

3. The reaction occurs by a synchronous mechanism when the high rate of chemical conversion is provided by the synchronous interaction of reagents in the coordination sphere of the SBMS. In this way a high degree of compensation for the energy consumed on activating the reagents is achieved by the energy evolved on adsorption and hydrogenation of the thiophene ring.

The proposed mechanism for the hydrogenolysis of thiophene explains the occurrence of a synergistic effect. The clearly defined, non-additive increase in the chemical reaction rate on bimetallic in comparison with monometallic sulphide catalysts is explained by the formation of a new chemical compound, an SBMS, which combines the qualities of monometallic catalysts in relation to the activation of the reactants, viz. the activation of H_2 on $MoS_2(WS_2)$, the lability of the Ni(Co)–S bond and the transfer of the activated hydrogen to the adsorbed thiophene molecule by direct metal–metal reaction between the dissimilar atoms.

A synchronous mechanism for the interaction of reactants in the coordination sphere of a metal has been discovered most frequently in heterogeneous catalysis.[92] Thus, for example, partially and completely oxidised traditional molybdenum oxide catalysts, prepared through the synthesis of surface metal complexes, conduct the oxidation of H_2 and CO [141,142] and propylene[143] by a synchronous mechanism. Their activity and selectivity is appreciably higher than for the analogous catalysts prepared by the impregnation method. It may be suggested that the synchronous mechanism is more widespread in heterogeneous catalysis than has been considered until now. The main difficulty in detecting it is seemingly the non-uniformity of the chemical composition of the surface of solid catalysts, since in several cases the appearance of particular intermediates may be caused by an alternative reaction route having no direct relation to the mechanism being examined.

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