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The Nature of the Active Component in Deposited Sulphide Catalysts

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The use of various physical methods (high resolution electron microscopy, Mössbauer spectroscopy, X-ray photoelectron spectroscopy, X-ray radial distribution of atoms, infrared spectroscopy, and the study of the long-range fine structure of X-ray absorption) for the elucidation of the structure of the active component in deposited sulphur catalysts is examined. The data obtained by these methods show that the active component in the catalysts considered has an MoS_2 (or WS_2) layer structure, while cobalt (or nickel) ions are distributed on the lateral faces of the dispersed sulphide particles.
The bibliography includes 63 references.

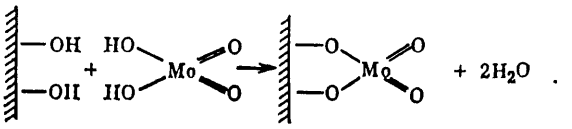
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I. INTRODUCTION

The catalysts used in practice usually consist of a complex mixture of bulk-phase and surface compounds. As a rule the catalytically active centres are incorporated in highly dispersed phases. The composition of the catalyst varies under the influence of the reaction medium. All these factors are responsible for the difficulties which arise in the solution of the problem of which of the compounds (or their combination) is essential for the manifestation of catalytic activity (i.e. is an active component of the catalyst). For the majority of the important industrial catalysts, this problem is still controversial. The most likely controversy in recent years arose in the discussion of the mechanism of the action of hydro-purification catalysts. Industrial catalysts for the refining of petroleum products by treating them with hydrogen at high temperatures contain molybdenum (or tungsten) compounds combined with cobalt (or nickel) compounds in a highly dispersed state on a carrier (alumina). Under the conditions of the reaction medium, the catalysts combine with sulphur (the formation of surface metal sulphides). In the course of hydro-purification at high temperature (350–450 °C) under a high hydrogen pressure (50–100 atm), C–S, C–N, and C–O bonds undergo hydrogenolysis (which leads to the removal of hetero-atoms from the petroleum products—in the first place the removal of sulphur in the form of hydrogen sulphide), metallic impurities are removed from the petroleum crude, and hydrogenation and isomerisation processes take place. Hydro-purification is one of the largest-scale catalytic processes (hundreds of millions of tonnes of petroleum products are processed). The annual production of hydro-purification catalysts runs into tens of thousands of tonnes. The scale of the employment of hydro-purification processes and of the manufacture of catalysts for this purpose will increase with increasing extent of the processing of petroleums having a high sulphur content (and, in future also, of the liquid products of the processing of coal). For example, in the USA these catalysts occupy the first place as regards the rate of growth of production and sales.[1–3] Industrial hydro-purification catalysts contain 12–20% of transition metal oxides on a carrier. The cost of the metals forming part of the composition of these catalysts is rapidly increasing. For example, the world prices of cobalt rose by a factor of 4 during the period from 1970 to 1976.[4] This makes it necessary to create active and stable catalysts with a low metal content. For the solution of this problem, it is important to understand the nature of the active component in the catalyst. Nevertheless, there is no unanimous view in the literature concerning the nature of such a component in sulphide catalysts. The most important of the proposed hypotheses are illustrated in Figs. 1–4.

The monolayer model (Fig. 1) has been put forward by Lipsch and Schuit[5] to account for the structure of the active component in hydrosulphurisation catalysts and improved models of this type have been considered in other studies.[6,7] This model is based on the hypothesis that surface oxide sulphides are formed in the monolayer of the surface aluminium molybdate when the latter combines with sulphur. The molybdate is produced in accordance with the mechanism



Cobalt is located within the Al_2O_3 lattice, but its role in the catalytic process remains obscure.

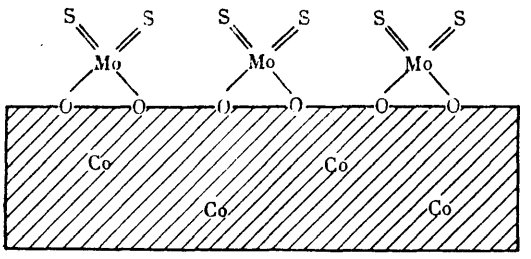


Figure 1. The monolayer model designed to account for the structure of the active component in hydrodesulphurisation catalysts.[5–7]

The intercalation model (Fig. 2) has been proposed by Voorhoeve and Stuiver[8] and improved by Farragher and Cossee.[9] According to this model, different metal ions can be inserted (intercalated) between sulphide packets linked by weak van der Waals forces. Farragher and Cossee[9] believe that intercalation of the Ni(Co) ions between

$MoS_2(WS_2)$ layers is confined to the surface of the lateral face. Thus the active centre is produced on the lateral face of the sulphide crystal; there is also a possibility of the formation of bimetallic active centres, including those incorporating Mo^{3+} and W^{3+} ions after the partial elimination of sulphur from the surface layer. Fig. 2 illustrates schematically the structure of the MoS_2 layer crystals; a similar scheme is valid for WS_2. The crystals of these sulphides consist of packets having the composition MS_2 and each packet comprises a layer of metal (M) atoms and two layers of sulphur atoms. A metal atom within the layer is coordinated to six sulphur atoms.

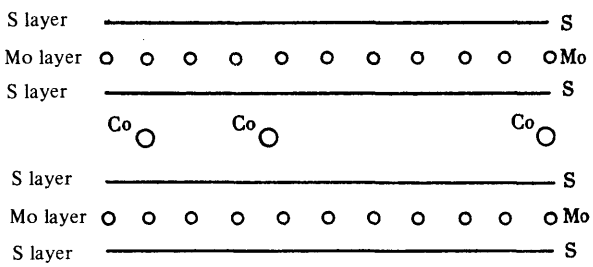


Figure 2. The intercalation model.[8,9]

The contact synergism model, proposed by Delmon and co-workers,[10-12] presupposed (Fig. 3) that two separate (albeit very disperse) sulphide phases are formed in mixed sulphide catalysts. These phases are in contact or are close to one another on the carrier. The active centres proper are distributed on the MoS_2 phase. The presence of cobalt sulphide activates the hydrogen.

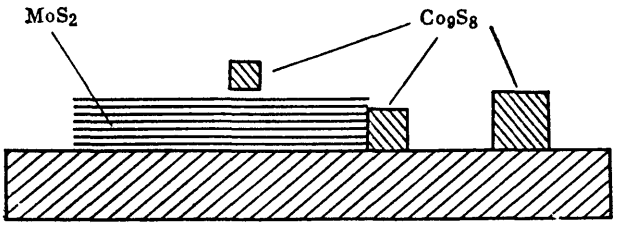


Figure 3. Delmon's "contact synergism" model.[10-12]

The insertion model has been put forward recently by Ratnasamy and Sivasanker.[13] In this model it is assumed that the cobalt atom is located on the lateral face of the MoS_2 crystal. Fig. 4 illustrates the lateral face of a single MoS_2 packet with inserted cobalt atoms. This model was put forward[13] without experimental justification on the hypothesis that the location of cobalt on the lateral face decreased the excess charge on the sulphur atoms adjoining the lateral face.

The application of a combination of physical methods has led in recent years to significant progress in the elucidation of the composition of the active component of hydropurification catalysts. The aim of the present review is not a complete retrospective consideration of all the data obtained in the study of hydrodesulphurisation catalysts (frequently extremely contradictory), since many excellent reviews covering this field already exist (see, for example, Refs. 13–17). Here we shall deal with the results of recent studies of two catalytic systems: $(Ni+W)/SiO_2$ (studies performed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[18-36]) and $(Co+Mo)/Al_2O_3$ (studies carried out by Topsøe and co-workers[14,37-54]).

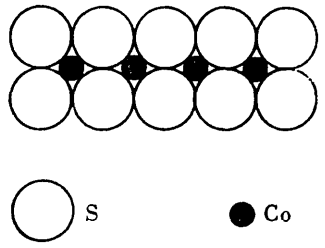


Figure 4. The insertion model.[13]

II. RESULTS OF THE STUDY OF THE $(Ni+W)/SiO_2$ SYSTEM

1. Characteristic Features of the Preparation of the Catalysts

Silica gel was used as the carrier for the preparation of the catalytic system, because it ensures a more uniform surface composition (compared with catalysts based on Al_2O_3) and a lesser degree of interaction of the deposited components with the carrier.

In order to attain the maximum degree of dispersion of the sulphide particles, the surface sulphides were obtained from attached organometallic complexes. The preparation of the catalyst is illustrated schematically in Fig. 5.

The preparation of catalysts incorporating only one metal (such catalysts are referred to below as monometallic) involved states in which the allyl complexes of tungsten and nickel interacted with the surface hydroxy-groups, the resulting attached complexes were treated with hydrogen, and the reduced forms of nickel (finely dispersed metallic nickel) and tungsten (W^{2+} ions) were subsequently converted into sulphides. The catalysts obtained in this way (henceforth such catalysts will be referred to as organometallic) were 5–20 times more active than the catalysts prepared by the standard method involving impregnation with $Ni(NO_3)_2$ and $(NH_4)_2WO_4$ solutions.[18,31] This difference in activity is associated mainly with the higher degree of dispersion of the sulphide particles and catalysts prepared from organometallic complexes (organometallic catalysts).

The monometallic sulphide catalysts Ni/SiO_2 and W/SiO_2 (the sulphur incorporated in the catalysts when it combines with them will not be indicated in the formulation of the catalyst composition either here or henceforth) exhibited approximately equal activities in the hydrogenolysis of thiophen at 300–350 °C. Analogous data indicating similar activities of cobalt and molybdenum sulphide deposited on charcoal have been published by De Beer et al.[55] Thus it

would not be useful to regard the sharp increase in the activity of the mixed sulphide systems (such systems are referred to below as "bimetallic") as "promotion" (this term is suitable for the case where one of the components is inactive or its activity is low). The mutual enhancement of activity in mixed sulphide systems is usually treated in the literature as a manifestation of synergism.

The most active bimetallic catalysts on SiO_2 have been obtained when the second component was deposited in the form of an organometallic compound on the dispersed sulphide of the first component (see Fig. 5). It is important to note that the $(Ni+W)/SiO_2$ sulphide catalysts of "organometallic" origin were more active than catalysts of analogous composition on alumina.[31]

The activity of the catalysts depends on the atomic ratio of the deposited metals (Fig. 6). The dependence of the overall activity a on $\lambda = Ni/(Ni+W)$ is analogous for organometallic hydrodesulphurisation catalysts and the specimens obtained by the usual procedures.[10,42,56]

The maximum activity per unit weight of the deposited metals in the "organometallic" catalysts is observed at $\lambda \cong 0.3$; the activity referred to 1 g of nickel increases with decrease of its content and reaches a maximum at $\lambda \leq 0.2$. Presumably for these values of λ the entire nickel (or at least a constant fraction of the latter) is incorporated in the composition of the active centres. We may note that analogous results have been obtained for the $(Ni+Mo)/SiO_2$ system.[24]

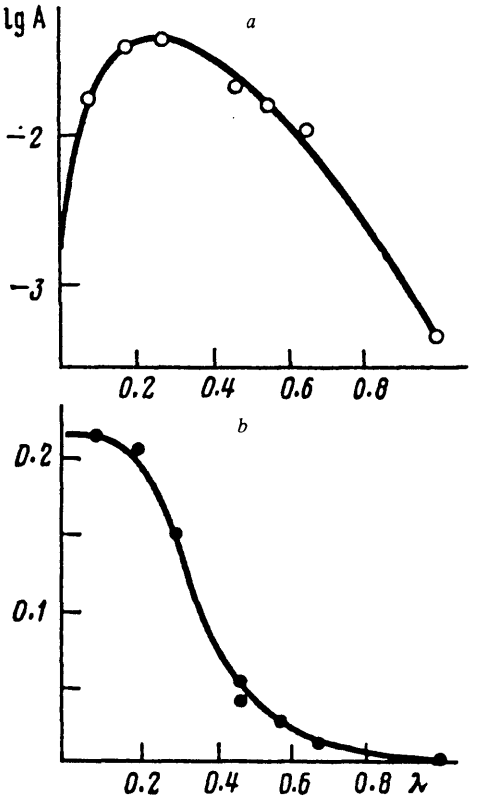


Figure 6. Dependence of the catalytic activity of the $(Ni+W)/SiO_2$ sulphide catalysts on the atomic ratio $\lambda = Ni/(Ni+W)$; the activity was measured in the hydrogenolysis of thiophen at 350 °C and 20 atm: *a*) activity (rate of reaction) referred to 1 gram-atom of both metals (Ni + W) (10^2 mol s^{-1}); *b*) activity referred to 1 gram-atom of nickel (10^2 mol s^{-1}).

2. High Resolution Electron Microscope Data

The morphology of the sulphide particles in the $(Ni+W)/SiO_2$ catalysts has been investigated[22,24,32] with the aid of a JEM-100CX electron microscope with a point resolution of 2 Å (Figs. 7 and 8). The photomicrographs of the monometallic Ni/SiO_2 and W/SiO_2 sulphide catalysts obtained from organometallic complexes show, against the background of SiO_2 globules, individual particles with dimensions <10 Å.

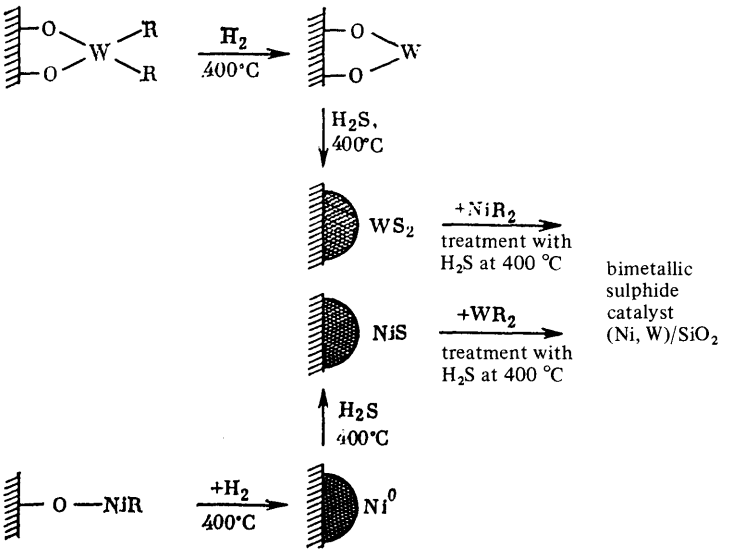


Figure 5. Schematic illustration of the preparation of deposited mono- and bimetallic catalysts using organometallic complexes.

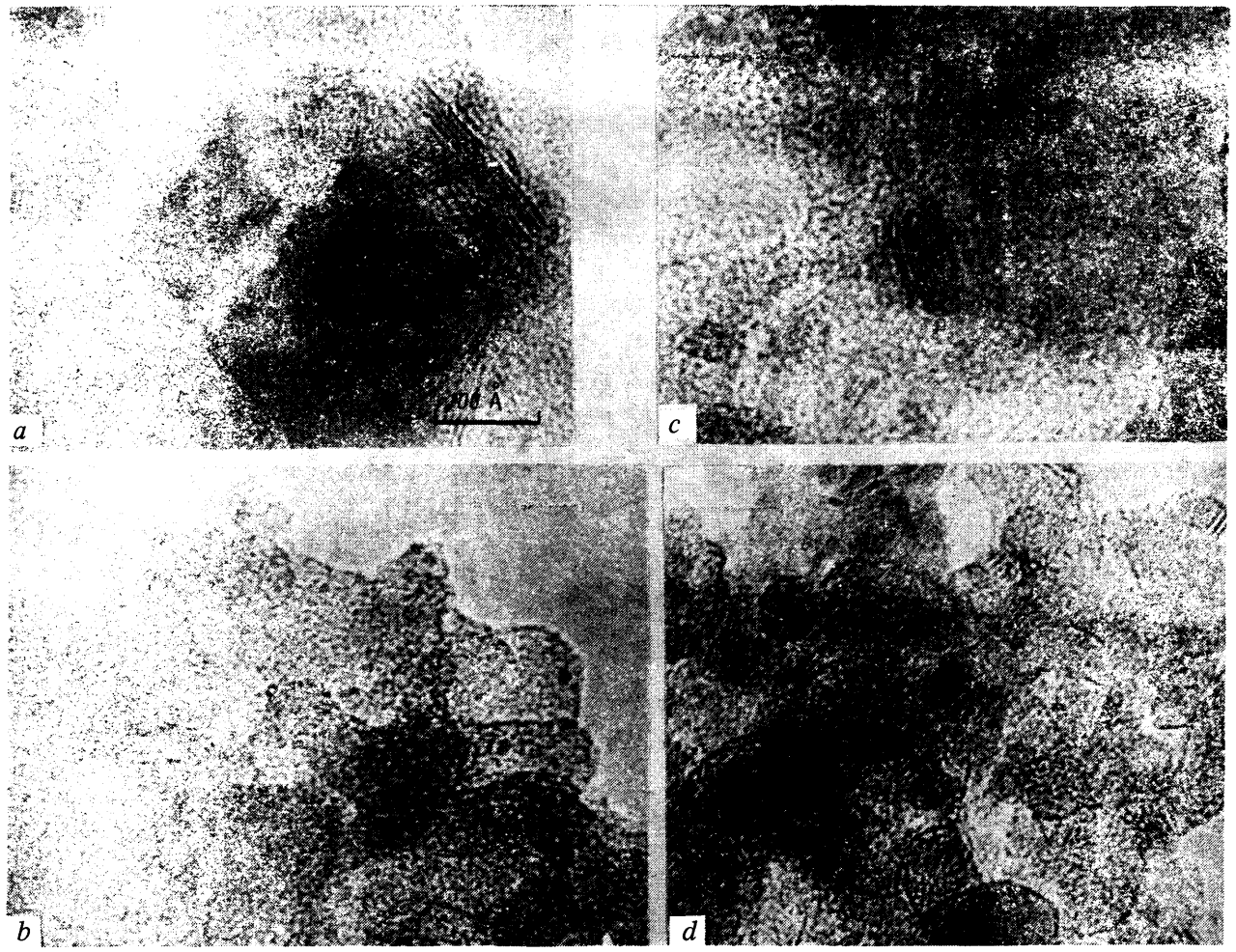


Figure 7. Electron photomicrographs of deposited sulphide catalysts: *a*) WS_2/SiO_2 catalyst obtained by the standard impregnation method; *b*) W/SiO_2 catalysts obtained from organometallic compounds fixed to the carrier; *c*) $(Ni+W)/SiO_2$ catalysts obtained by the standard method involving simultaneous impregnation with aqueous $Ni(NO_3)_2$ and $(NH_4)_2WO_4$ solutions; *d*) $(Ni+W)/SiO_2$ catalyst obtained by treating a W/SiO_2 specimen with the allyl complex of nickel and subsequent sulphiding at 400 °C.

In the case of catalysts obtained by "standard" impregnation methods, particles of nickel and tungsten sulphides can be seen. Thus the photomicrographs of the catalyst containing WS_2 show formations whose size ranges from 20 to several hundred angstroms. These agglomerates have a layer structure with interlayer distances of ~6 Å, which corresponds to a distance $d_{002} = 6.2$ Å between individual layers of tungsten atoms in the WS_2 crystal. Comparison of the dimensions of the sulphide particles in the "standard" and "organometallic" catalysts shows that the higher activity of the latter can be accounted for in the main by the higher degree of dispersion.[22,32]

A different morphology of the surface particles is characteristic of the bimetallic sulphide catalysts compared with that of the monometallic W/SiO_2 specimens of "organometallic" origin. Instead of particles approximately 10 Å in size, linear structures (strips) 20–50 Å long appear in the sulphur-treated $(Ni+W)/SiO_2$ catalyst. The photomicrographs of the "organometallic" specimens show mainly single strips; when packets of strips are formed, the distance between the strips "layers" is about 6 Å. Evidently the individual strips are projections of the WS_2 layers onto the lateral surface.

The numbers of layers in the surface particles of the "organometallic" and "standard" catalysts differ significantly (Fig. 8). The dominant type of particles in the most dispersed organometallic catalyst consist of single-layer formations. In the "standard" catalysts the sulphide particles contain 6–10 layers.[32] Comparison of the activities of the "organometallic" and "standard" catalysts with the morphology of the sulphide particles in them provides evidence in support of the view that the active centres are located on the lateral faces of the sulphide particles (Fig. 9). The activity of the "organometallic" catalysts is ~3 times higher than that of the "standard" catalysts. We shall assume that the active centres are located on the basal plane. In this case a greater difference should be observed between the activities, since, on passing from the "organometalic" to "standard" specimens, the fraction of the surface of the basal planes per unit mass of the active phase (and

hence the catalytic activity) should fall approximately in proportion to the increase of the number of layers in the particles of the surface sulphide.

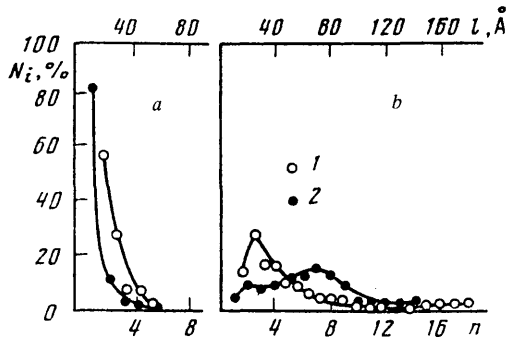


Figure 8. Distribution of particles with respect to size in the $(Ni+W)/SiO_2$ sulphide catalysts according to electron microscope data: *a*) catalyst obtained from organometallic compound; *b*) catalyst obtained by the standard impregnation method; *1*) length of layers *l*; *2*) number of layers *n*; N_i = fraction of particles (%).

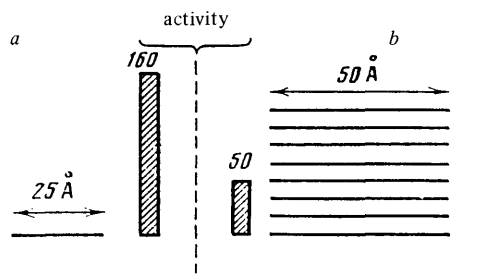


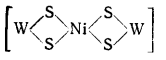
Figure 9. Comparison of the typical surface structures in the deposited sulphide catalysts $(Ni+W)/SiO_2$ according to electron microscope data; the lines correspond to individual WS_2 layers; the catalytic activity is expressed as the rate of hydrogenolysis of thiophen at 350 °C [10^{-4} mol (Ni + W g-atom)$^{-1}$ s^{-1}]: *a*) catalyst obtained from organometallic compounds; *b*) catalyst obtained by the standard impregnation method.

It follows from the results that (a) layer structures characteristic of massive WS_2 or MoS_2 sulphides are formed in the bimetallic sulphide catalysts. The most dispersed "organometallic" catalysts with an enhanced activity contain single-layer formations (single packets). This finding is inconsistent with the intercalation model[8,9] which presupposes not less than two layers of packets for the formation of active centres. (b) The most probable site at which the active centres for the hydrogenolysis of the C–S bond are located on the lateral faces of WS_2 or MoS_2 crystals.

The results of electron microscope studies do not, however, permit an unambiguous conclusion about the formation of mixed compounds from nickel and tungsten sulphides.

3. X-Ray Photoelectron Spectroscopic (XPES) Data

When dispersed nickel or tungsten (molybdenum) sulphides are formed on the surface of silica gel, an appreciable increase of the electron binding energy E_b at the $Ni2p_{3/2}$ and $W4f_{7/2}$ levels is observed in the XPE spectra (Fig. 10) compared with the massive sulphides.[19,33] This indicates the interaction of the dispersed sulphides with the carrier with a consequent decrease of the electron density on the deposited metals. When mixed catalysts are prepared, a further increase of E_b at the $Ni2p_{3/2}$ levels and a decrease of E_b at the $W4f_{7/2}$ and $(Mo3d_{5/2})$ levels takes place. Thus the introduction of nickel into the composition of dispersed sulphide catalysts leads to its interaction with tungsten (molybdenum), which entails the transfer of electron density from nickel to W(Mo) atoms. We may note that the absolute values of E_b at the $Ni2p_{3/2}$ and $W4f_{7/2}$ levels for the catalysts and the thiotungstate and thiomolybdate complexes containing the $[Ni(MS_4)_2]^{2-}$ anion, where M = Mo or W, are similar. In these compounds nickel is surrounded by sulphur atoms:



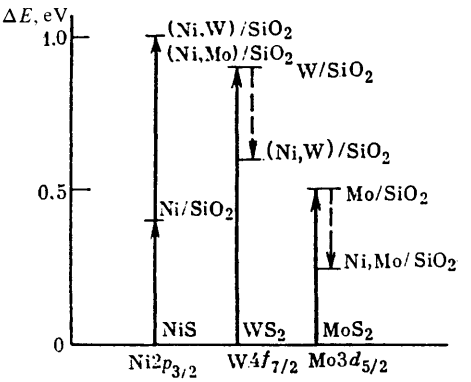


Figure 10. The change in the energies of the $Ni2p_{3/2}$, $W4f_{7/2}$, and $Mo3d_{5/2}$ electronic levels in deposited mono- and bi-metallic sulphide catalysts relative to the NiS, WS_2, and MoS_2 massive sulphides.

Thus the application of the XPES method established that mixed sulphide compounds are indeed formed in the bimetallic catalysts. In order to elucidate the structure of the mixed compounds produced, it is necessary to resort to structural data.

4. Data Obtained by Structural Methods

Deposited sulphide catalysts obtained from attached organometallic compounds are amorphous to X-rays. Information about the interatomic distances in the highly dispersed particles of the deposited catalysts can be obtained by the X-ray atomic radial distribution (XARD) method.[57,58] The XARD curves for deposited sulphide catalysts are presented in Fig. 11. The following interatomic distances, which are satisfactorily correlated with the values characteristic of WS_2, have been determined for the $(Ni+W)/SiO_2$

sulphide catalysts:[34] ~2.5 Å (W–S distances in the WS_2 layer amounting to 2.48 Å; ~3.2 Å (W–W distance amounting to 3.187 Å); ~4.1 Å (distance between the W atoms and the S atoms in the second coordination sphere amounting to ~4.04 Å). At the same time the XARD curves for the deposited catalysts show a peak at ~3.8 Å, which was not observed in the study of the WS_2 structure.

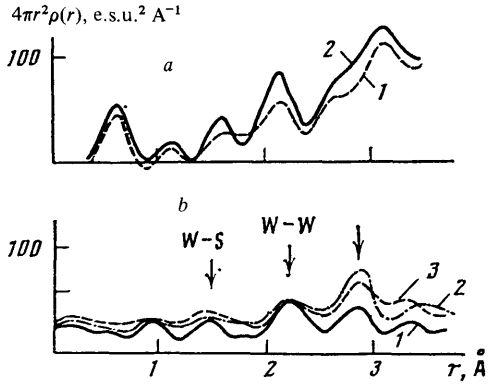


Figure 11. *a*) radial distribution curves for the carrier (SiO_2) (curve *1*) and the sulphur-treated W/SiO_2 catalyst prepared from organometallic precursors (curve *2*); *b*) differential radial distribution curves for the sulphur-treated catalysts obtained after subtracting the curve corresponding to the carrier: *1*) W/SiO_2 specimen obtained from organometallic precursors; *2*) $(Ni+W)/SiO_2$ specimen obtained from organometallic precursors; *3*) $(Ni+W)/SiO_2$ specimen obtained by the standard impregnation method.

The same interatomic distances have been found for the bimetallic sulphide catalysts as for the monometallic catalysts. Thus the surface compounds in the deposited W/SiO_2 and $(Ni+W)/SiO_2$ sulphide catalysts have the structure of massive WS_2. An analogous conclusion is valid for the deposited molybdenum catalysts.

The introduction of nickel does not entail the appearance of new peaks on the X-ray plots (or XARD curves) for the deposited sulphide; only the intensities of certain maxima, characteristic of the W/Si_2 catalysts, increases. The increase of the intensity of the maxima can also be associated with the formation of WS_2 layers ~25 Å long (instead of the more dispersed formations).

If nickel ions are intercalated between WS_2 layers, one might have expected the appearance of the maximum corresponding to an Ni–W distance of 3.45 Å. Since this peak was not observed, one may conclude that intercalation compounds are not formed in the mixed sulphide catalysts; the Ni–Ni distance characteristic of nickel sulphides (3.4 Å) is also absent.

It is noteworthy that the peaks corresponding to the W–W distances between the atoms in different packets of the WS_2 structure are not manifested on the XARD curves for the deposited sulphide catalysts. These results are consistent with electron microscope data, according to which single WS_2 packets are formed preferentially on the surface and, when aggregates are produced, the layers in the latter are not arranged in parallel.

The appearance of a maximum of 3.8 Å, which does not correspond to the interatomic distances in the WS_2 structure, has been explained[34] by the appearance of a chemical bond between the deposited sulphides and the carrier with formation of Si–O–W–S fragments. In these fragments the Si...W distance is ~3.8 Å. Comparison of the WS_2 structure with that of the SiO_2 surface layers shows that the W–W and S–S interatomic distances in WS_2 are close to the O–O interatomic distances in two neighbouring SiO_4 tetrahedra forming the SiO_2 structure. The surface layer sulphide compounds of tungsten can therefore be formed without distorting the structure of the layer.

Thus it follows from the XARD data that (a) the WS_2 layer structure is retained in the deposited sulphide catalysts without the formation of a regular three-dimensional structure; (b) the appearance of the maximum corresponding to an interatomic distance of 3.8 Å, which is not observed in WS_2 and SiO_2, may be due to the formation of chemical bonds between the deposited sulphides and silica gel.

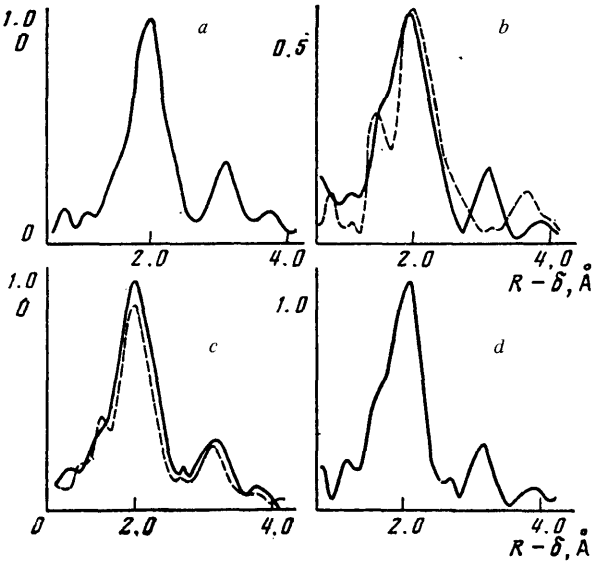


Figure 12. Radial distribution curves obtained by the EXAFS method in the measurement of the L_{III} spectrum of tungsten in the sulphided catalysts: *a*) massive WS_2 sulphide; *b*) W/SiO_2; *c*) $(Ni+W)/SiO_2$, $\lambda = 0.3$; *d*) $(Ni+W)/SiO_2$, $\lambda = 0.5$; the dashed lines correspond to specimens brought into contact with air; U = relative intensity (arbitrary units); R = interatomic distance; δ = phase shift.

Additional data for the structure of the surface sulphide compounds have been obtained by the EXAFS method (the principles of the method in relation to the study of catalysts have been described by Mastikhin and Zamaraev[59]).

In order to determine the interatomic distances characteristic of the environment of the tungsten atom, the L_{III} absorption spectra of this element have been recorded.[35] The radial distribution curves are illustrated in Fig. 12. Peaks corresponding to the W–S (~2.46 Å) and W–W (~3.19 Å) interatomic distances characteristic of the WS_2 packet were found for the W/SiO_2 catalyst. A maximum at $R-\delta = 1.61$ Å was also observed, which may be due to the presence of oxygen in the coordination spheres of the tungsten ions (Si–O–W fragments linking the ultradispersed particles of tungsten sulphide to the carrier

surface). The introduction of nickel into the composition of the catalyst increases the intensity of the peaks at $R-\delta = 2.05$ and 3.09 Å. It has been suggested[35] that this may be caused by the additional scattering by nickel ions. When account is taken of the phase correction for the scattering by nickel ions, the W–Ni distances should be 2.38 and 3.42 Å in this case. Analysis of the *K* absorption spectra of the nickel in the mixed sulphide catalyst showed that there are sulphur ions in the immediate environment of nickel. The Ni–S distance is 2.22 Å, which is significantly less than the Ni–S distance in α-NiS (2.38 Å). These data confirm the conclusion that the Ni–S phase is absent from the bimetallic catalysts. The Ni–S distance of 2.22 Å is close to that characteristic of the Ni–S bond length in $[Ni(WS_4)_2]^{2-}$, where the nickel is present in a planar square made up of sulphur ions.

5. The Structure of the Active Component of the $(Ni+W)/SiO_2$ Sulphide Catalyst

By the active component, we understand surface structures containing the active centres for the catalytic reaction. The active centre should be understood as the minimum number of surface atoms necessary for the occurrence of the catalytic cycle.

When models of the active component and of the active centre in deposited sulphide hydrosulphurisation catalysts are considered, account must be taken of the following experimental facts observed in the course of the investigation of the $(Ni+W)/SiO_2$ system prepared from organometallic compounds: (a) highly dispersed sulphide particles are present on the catalyst surface mainly in the form of monolayer structures comprising individual packets with linear dimensions of ~25 Å; (b) mixed compounds of two metals (nickel and tungsten in the case considered) are formed on the surface; (c) the interatomic W–S (2.46 Å) and W–W (3.20 Å) distances in the highly dispersed sulphide particles correspond to the layer structure of the massive tungsten sulphide; (d) maxima, which can be referred to the W–O (1.93 Å) and Si–W (3.8 Å in the Si–O–W fragment) distances, are observed on the radial distribution curve; (e) sulphur ions are present in the first coordination sphere of nickel at a distance of ~2.22 Å. Nickel ions are apparently distributed at distances of 2.32 and 3.42 Å from the tungsten ions.

It follows from the data obtained that the active component has the layer structure typical for WS_2 (or MoS_2) crystals. The active component may be a single packet comprising two layers of sulphur atoms and a layer of W (or Mo) atoms between them. This packet can be arranged either parallel to the carrier surface [can adjoin the carrier via its basal plane (Fig. 13*a*)] or at right angles to the surface, i.e. can adjoin the carrier via its lateral face (Fig. 13*b*). According to electron microscope data, the second possibility is more likely. A cross section for such a packet is illustrated in Fig. 14. Some of the tungsten atoms are linked to the oxygen atoms on the carrier surface. The appearance of the more negative (compared with sulphur) oxygen in the coordination sphere of the tunsten ion leads to a difference between the positions of the electronic levels of tungsten in the dispersed surface particles compared with massive WS_2. The nickel atoms are located on the lateral face of the active component, being distributed in the same plane as the tungsten atoms. Fig. 14 illustrates two possibilities for the adsorption of a thiophen molecule: on a bimetallic active centre (Fig. 14*a*), after the removal of a single sulphur atom from the surface of the active component, and on a monometallic active centre (Fig. 14*b*).

The structure presented in Fig. 13*b* contains Si–O–W fragments with an Si–W distance of ~3.8 Å, which corresponds to the peak on the XARD curve.

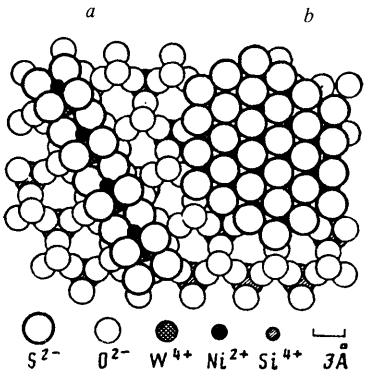


Figure 13. Distribution of the WS_2 packets on the silica gel surface: *a*) packet arranged at right angles to the SiO_2 surface, adjoining it via its lateral face; *b*) packet in contact with the SiO_2 surface via its basal plane.

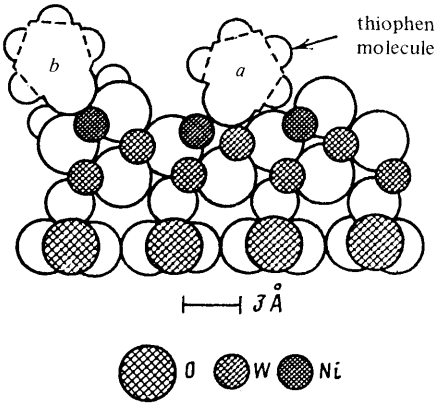


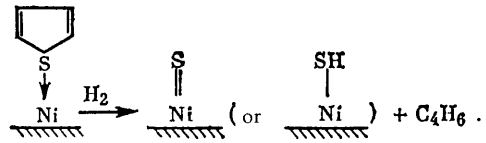
Figure 14. The possible structure of the active component in the sulphide hydrodesulphurisation catalysts.

In the study of the structures of the active centres on sulphide catalysts, it is important to determine the location of the nickel (or cobalt) ions in the layer structure of the active component. The possible structures formed when the nickel atoms are distributed on the lateral face of the WS_2 crystal have been examined in detail.[36] The best correspondence with structural data has been observed on the hypothesis that the nickel atom substituting a tungsten atom is surrounded by sulphur atoms on the lateral face (Fig. 14). Findings such as the appearance of shortened Ni–S distances and two types of interatomic Ni–W distances can then be explained.

We shall examine the possible types of active centre.

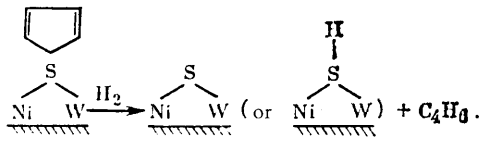
(a) A monometallic active centre—a coordination-unsaturated nickel ion. After the adsorption of thiophen and its hydrogenolysis on such a centre, the sulphur atom is bound

to one metal ion:



The role of tungsten sulphide then reduces to providing the lateral faces of its crystal as a matrix for the accommodation of the coordination-unsaturated nickel ions.

(b) A bimetallic active centre. In this case WS_2 plays the role not only of the matrix for the stabilisation of the nickel ions but also participates directly in catalysis. In the course of the hydrogenolysis of thiophen, a sulphur atom is bound to two metal ions:



It has been shown[36] that the removal of surface sulphur, bound to two metal atoms, require a significantly greater energy expenditure than the removal of the sulphur bound to one nickel (or cobalt) atom. The successive removal and addition of sulphur to the monometallic active centre in the catalytic cycle is therefore more likely. The existence of the optimum ratio $\lambda = Ni/(Ni+W) = 0.3$ can be explained with the aid of the above model of the binding of nickel ions on the tungsten sulphide surface. The above value is close to the atomic fraction of the nickel stabilisation centres on the lateral faces of tungsten sulphide packets with a size of 20–50 Å. When the nickel content is above the optimum value, the activity falls (for example, down to 10% of the maximum activity for $\lambda = 0.6$), apparently as a consequence of the shielding of the active centres by nickel sulphide.

The model of the active component considered above has certain features of the "monolayer model" (retention of the bond between the sulphide species and the carrier), the Cossee model (distribution of the ions of the second metal on the lateral face of the sulphide), and the Ratnasamy "insertion" model (distribution of nickel on the lateral plane of a single sulphide packet; square coordination of the nickel ion), but is inconsistent with Delmon's synergistic model (Fig. 3). The results of the study of the $(Ni+W)/SiO_2$ system confirmed the principal postulates of the hypothesis put forward by Topsøe concerning the nature of the active component on cobalt plus molybdenum sulphide/alumina desulphurisation catalysts.

III. RESULTS OF THE STUDY OF THE $(Co+Mo)/Al_2O_3$ SYSTEM

The $(Co+Mo)/Al_2O_3$ system is used widely as an industrial hydropurification catalyst (nickel is sometimes used instead of cobalt). The catalysts are usually prepared by the successive impregnation of the carrier with aqueous solutions of the components followed by heat treatment in air at 500 °C and conversion into the sulphide form. A number of studies have been made on this system (see the relevant reviews[14–17,53]), but these did not yield unambiguous data owing to the inhomogeneity of the surface composition of the given system (particularly in the oxidised state) and the high degree of dispersion of the active component. As a result of the systematic studies by Topsøe and co-workers[14,37–54] by various physical methods, more reliable information about the nature of the active component in this system has been obtained only in recent years.

1. Mössbauer Emission Spectroscopic Data

Systematic application of this method to the study of sulphide systems yielded important information about the nature of the active component in the system considered. It has been noted[14,39] that this is associated with the following features of the method: (a) the Mössbauer parameters (the isomer shift δ, the quadrupole splitting ΔE_Q) are very sensitive to the oxidation state and the composition of the immediate environment of the element investigated; (b) Mössbauer spectra can be measured directly under reaction conditions (at an elevated temperature and in the reaction medium with the necessary composition).

The principal data have been obtained using Mössbauer emission spectroscopy (MES). In the study of sulphide catalysts, mainly specimens into which ^{57}Co had been introduced were used. The details of the method have been described in detail elsewhere.[38,39,60] The advantage of the MES method compared with another method [X-ray photoelectron spectroscopy (XPES)] which makes it possible to obtain information about the electronic state of a given element, are evident from a comparison of the spectra (Fig. 15). Whereas the XPE spectra of metallic cobalt and its compounds are virtually identical, the ME spectra differ sharply.

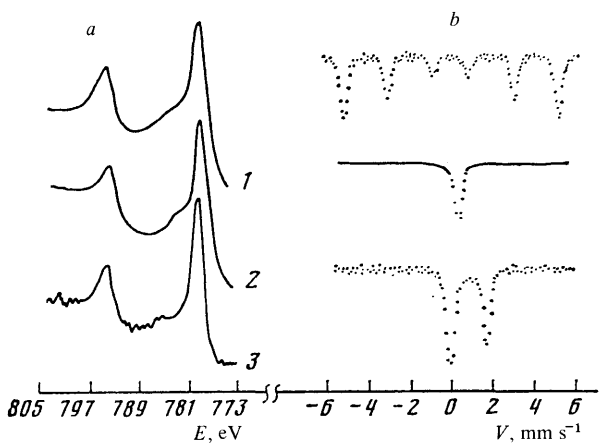


Figure 15. X-Ray photoelectron Co2*p* spectra (*a*) and Mössbauer absorption spectra of the individual compounds (b); E = bond energy (eV); V = velocity; *1*) metallic cobalt; *2*) Co_9S_8; *3*) $CoMo_2S_4$.[14]

In the first studies[37,38] involving the application of MES, the authors already concluded that in the cobalt–molybdenum sulphide catalysts cobalt is present in a compound different from Co_9S_8 and $CoMo_2S_4$; the compound has been called the "Co–Mo–S phase". The ME spectrum of this phase is characterised by a doublet Q_1 (Fig. 16), whose parameters differ from those of the individual compounds. The spectra of the sulphide catalysts show, together with the doublet Q_1, a weak signal (a doublet Q_2) corresponding to the same state of cobalt in which it existed before being converted

into the sulphide (apparently these are cobalt ions bound to the carrier).

A detailed study of the formation of the "Co–Mo–S phase" as a function of the composition and conditions in the preparation of the catalysts[40–48] permitted the following principal conclusions:[47,53]: (a) the "Co–Mo–S phase" is not a stoichiometric compound of definite composition; (b) the cobalt atoms in the "Co–Mo–S phase" are surrounded by sulphur atoms; (c) the "Co–Mo–S phase" is present in both deposited catalysts, obtained using various carriers (Al_2O_3, SiO_2, activated charcoal), and in massive mixed catalysts; (d) the cobalt atoms are present on the surface, since their environment changes after the adsorption of oxygen; (e) there is a correlation between the content of the "Co–Mo–S phase" in both deposited and massive catalysts and the catalytic activity in hydrodesulphurisation.

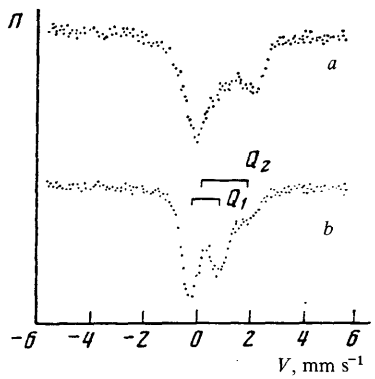


Figure 16. Mössbauer emission spectra of the $(Co+Mo)/Al_2O_3$ catalysts:[42] *a*) catalyst in the oxidised state; *b*) after treatment with the H_2S+H_2 mixtures; П = absorption.

The content of the "Co–Mo–S phase" reaches a maximum for the optimum Co : Mo ratio. At low cobalt concentrations the fraction of this element entering into the composition of the "Co–Mo–S phase" is close to 100%; with increase of the cobalt concentration, the fraction falls and the content of the inactive sulphide Co_9S_8 increases.[42]

2. X-Ray Photoelectron Spectroscopic Data

The position of the Co2*p* level in the cobalt catalysts deposited on molybdenum sulphide is higher by 0.5 eV than in massive Co_9S_8.[46] The position of the Co2*p* peak for the remaining catalysts is close to that characteristic of $Co_2Mo_2S_4$. This led to the conclusion that the electronic states of cobalt in the "Co–Mo–S phase" and in $CoMo_2S_4$ are similar. Thus cobalt is present in the mixed catalysts in the form of Co(II) in a low-spin state. This interpretation of the XPES data differs from that proposed by Brinen and Armstrong,[61] who concluded that metallic cobalt is present in the sulphide catalysts. The study of the XPE spectra of Co_9S_8 [46] and CoS_2 [62] showed that the absence of satellite peaks is characteristic of the state of Co(II) in the sulphide systems.

3. EXAFS Data

According to EXAFS data,[48] only one peak on the radial distribution curve is observed for the oxide catalysts Mo/Al_2O_3 and $(Co+Mo)/Al_2O_3$. The absence of a second ordered coordination sphere shows that the coordination of the molybdenum ions in the catalysts investigated is greatly distorted. As a result of the conversion of the catalyst into the sulphide phase, more regular structures are produced. Comparison of the EXAFS data for MoS_2 and the sulphided catalyst led to the conclusion[48] that molybdenum ions enter into the composition of the dispersed MoS_2 particles, whose size is independent of the presence of cobalt in the catalyst. In the same study the authors concluded that oxygen ions are absent from the coordination sphere of molybdenum (i.e. the oxide sulphide groups are not formed in the system considered). The immediate environment of cobalt ions contains sulphur atoms and there is no order in the second coordination sphere of the cobalt ions. The Co–S distance in the "Co–Mo–S phase" differs from that between the same atoms in Co_9S_8 or $CoMo_2S_4$. The composition of the coordination sphere of cobalt changes when the catalyst comes into contact with air.

4. Infrared Spectroscopic Data

Bands corresponding to the hydroxy-groups of the carrier are not observed in the infrared spectra of the catalysts sulphided at 320 °C.[49] Such groups are manifested in the spectra of catalysts sulphided at 600 °C. This indicates the formation of three-dimensional sulphide particles when the catalysts are subjected to a high-temperature treatment, which is also confirmed by electron microscope data. It is believed[50] that the absence of bands due to the OH groups of the carrier from the infrared spectra indicates the retention in the catalysts subjected to a low-temperature treatment (320 °C) of the bond between the active component and the carrier (although the character of this bond remains undefined).

The use of NO as the probe molecule in the study of the surface compounds in the $(Co+Mo)/Al_2O_3$ oxide catalysts revealed the formation of a mixed compound (the "Co–Mo–O phase"). This compound can apparently be regarded as the precursor of the active component formed after treatment with sulphur.[30] The intensity of the absorption bands of the NO adsorbed on the "Co–Mo–O phase" was proportional to the activity of the sulphided catalyst. The amount of adsorbed nitric oxide is also correlated with the catalytic activity.[29] It is noteworthy that the structure of the "Co–Mo–O phase" differs from that of cobalt molybdate.

The infrared spectra of the adsorbed nitric oxide make it possible to distinguish two types of adsorption centres in the sulphided $(Co+Mo)/Al_2O_3$ catalysts—on molybdenum and cobalt.[54] It was found that, with the increase of the cobalt content in the catalyst, the number of adsorption centres containing Mo ions falls. A correlation has been observed between the catalytic activity and the amount of nitric oxide adsorbed on cobalt ions. This permitted the important conclusion that cobalt ions enter directly into the composition of the active centres.

5. The Structure of the Active Component of the $(Co+Mo)/Al_2O_3$ Sulphide Catalyst

The MES and EXAFS data are inconsistent with the oxide sulphide and intercalation models and also the synergistic model. On the basis of the set of data obtained, Topsøe

and co-workers[14,50,54] proposed a model, according to which the active component (the "Co–Mo–S phase") consists of highly dispersed particles having the MoS_2 structure (usually a single-layer packet). The cobalt atoms are present on the lateral faces of these packets. According to Candia et al.[54], the cobalt atoms block the coordination-unsaturated molybdenum ions distributed on the lateral face. A structure of the active component corresponding in essence to the Ratnasamy model[13] has been put forward by Topsøe et al.[40] For a high degree of dispersion of the active phase (sulphide particle size ~10 Å), the maximum concentration of cobalt ions distributed on the lateral force of the MoS_2 crystal can correspond to a stoichiometry with Co : Mo ≅ 0.5.[40] An increase of the cobalt content above the optimum value entails the formation of the inactive sulphide Co_9S_8. In conformity with the model proposed by Topsøe and co-workers,[14,50,54] the increase of the activity of the catalyst as a consequence of the deposition of cobalt is associated with the formation of new centres. The degree of dispersion of the molybdenum sulphide particles does not change when cobalt is introduced into the catalyst and the "Co–Mo–S phase" is formed.

IV. CONCLUSION

The study of the (Ni + W)/SiO_2 and (Co + Mo)/Al_2O_3 catalytic systems of different composition by a combination of physical methods led various groups of investigators to similar conclusions concerning the nature of the active compounds in the hydrodesulphurisation catalysts: the active component in the sulphide catalysts consists of highly dispersed sulphide particles retaining the layer structure characteristic of the massive sulphides (MoS_2 or or WS_2); the active centres, incorporating the atoms of the second transition element (nickel or cobalt), are distributed on the lateral faces of the highly dispersed sulphides; the increased activity of the mixed catalytic systems is due to the formation of a surface compound containing the atoms of both transition elements. The atomic activity of the centres in the mixed catalysts is appreciably higher (apparently by about two orders of magnitude) than that of the centres in catalysts containing only one metal.

There is some discrepancy in the data obtained in the study of the above systems as regards the estimation of the degree of interaction with the carrier. For the (Ni + W)/SiO_2 catalysts obtained from organometallic compounds, there exist data demonstrating the retention of a bond between tungsten and the oxygen of the carrier. It may be that this is due to the method of preparation of the catalyst via the stage in which the organometallic complexes are fixed on the carrier. Oxygen atoms were not detected by the EXAFS method in the first coordination sphere of molybdenum in the (Co + Mo)/Al_2O_3 catalysts. However, one cannot rule out the possibility that a small number of chemical bonds between MoS_2 and the carrier are retained in this catalyst too, which is the reason for the retention of a high degree of dispersion of the deposited sulphides under severe conditions of the operation of the catalyst.

Thus important features of the active formations in the mixed sulphide catalysts were elucidated recently as a result of the application of a combination of physical methods. However, the role of the individual components of the catalyst remains obscure. Different causes of the promoting influence of Group VIII metals (M^{VIII}) added to Group VI metal (M^{VI}) sulphides have been discussed in the literature (see, for example, Pratt and Sanders[63]). These causes can be divided into two groups:

(1) The introduction of the metal M^{VIII} leads to the structural modification (an increase of the degree of dispersion and stability) of the sulphide $M^{VI}S_2$;

(2) The introduction of the metal M^{VIII} increases the number of the active centres in the $M^{VI}S_2$ phase (anionic vacancies, reduced M^{VI} ions) as a result of the activation of hydrogen.

Data obtained by electron microscopy[22,32] have shown that the introduction of nickel into the W/SiO_2 catalyst can increase the degree of dispersion of the sulphide particles, but this is not the main cause of the sharp increase of the activity of the mixed catalysts. An increase of the degree of dispersion of the sulphide particles as a consequence of the introduction of cobalt has not been observed in the Mo/Al_2O_3 system.[54]

The study of catalysts obtained by depositing $Ni(C_3H_5)_2$ on massive tungsten disulphide has shown[28,29] that the activity referred to one nickel atom is approximately constant regardless of the nickel concentration and also of the morphology and area of the WS_2 surface. The same atomic catalytic activity is characteristic of deposited catalysts at low nickel concentratons (below the optimum value of λ). This suggests that nickel enters directly into the composition of the active centres. There exist different views concerning the ions (M^{VI} or M^{VIII}) which constitute the centres for the activation of thiophen. A scheme for the hydrogenolysis of thiophen on the "Co–Mo–S phase", according to which thiophen is activated on molybdenum ions, has been put forward.[14] It has been suggested[14] that the presence of cobalt weakens the Mo–S bond, which facilitates the removal of sulphur under the reaction conditions with formation of coordination-unsaturated molybdenum ions on which thiophen is adsorbed. It has been concluded[54] that the active centres in the mixed sulphide catalysts incorporate directly the atoms of the Group VIII–VI element.

Analysis of the possible strength of the bonds between sulphur and surface centres of different composition has led to the hypothesis[36] that the active centre contains M^{VIII} ions. The layer sulphide $M^{VI}S_2$ serves as a matrix for the stabilisation of M^{VIII} in the sulphide environment. The role of the Group VI metal may also consist in altering the reactivity of the centre containing the M^{VIII} ion (for example, in facilitating the removal of the sulphur bound to M^{VI} as a result of the formation of the M^{VI}–M^{VIII} bond).

Despite the fact that significant progress has been made in recent years in the elucidation of the nature of the active component in sulphide hydropurification catalysts, a whole series of questions concerning the mechanism of the action of these catalysts still awaits an answer. One of these questions is why a specific combination of two metals (namely the location of cobalt or nickel in the layer structures of tungsten or molybdenum sulphides) actually ensures a high activity in the hydrogenolysis of the C–S bond. The mechanism of the activation of the C–S bond and of the hydrogen molecule on sulphide catalysts remains unelucidated. Further studies should provide an answer to these questions and should also yield additional data on the structure of the active centres in one of the most important classes of industrial catalysts—the hydropurification catalysts.

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