

BIMETALLIC SULPHIDE CATALYSTS Ni-M-S_x/SiO₂ PREPARED BY UNCONVENTIONAL METHOD INVOLVING THIOUREA COMPLEXES

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An unconventional method of preparation of hydrodesulphurization catalysts was tested. A series of M-S_x/SiO₂ and Ni-M-S_x/SiO₂ catalysts was prepared, where M was V, Cr, Mn, Mo, W or Nb, respectively. A mixture of a salt of the metal M, thiourea, glycerol, sulphur, isopropanol, and silica gel was thermally decomposed to obtain the M-S_x/SiO₂ catalysts. Nickel was deposited from solution of nickel acetate in methanol. Activity of catalysts was tested in benzothiophene hydrodesulphurization and their surface composition was characterized by XPS. The activity of samples containing Ni-Mo and Ni-W was in the rank of classical Co-Mo/Al₂O₃ catalysts but other samples exhibited only low activity and no synergism. The increase in binding energy of Ni after mixing with second metal M was observed not only for Mo and W but also for V, Cr, and Mn. It is concluded that this shift is probably not the main cause of synergism as suggested in the literature.

The well established industrial procedure of preparation of hydrorefining Co-Mo, Ni-Mo, and Ni-W sulphide catalysts is the impregnation of alumina support with oxo salts, calcination and *in situ* sulphidation. However, recent journal and patent literature pays an increased attention also to various alternative routes. In the standard impregnation method, the properties of resulting sulphide catalysts are strongly predetermined by structure of their oxidic precursors. It is possible that the chemistry of the oxidic stage of the catalyst limits the structure of the final sulphide; that may be the reason why a number of procedures which do not include this stage have been studied. The common characteristic feature of them is introduction of the sulphur species already in the moment of the formation of a first solid precursor of catalyst or in the moment of addition of active transition metal ions to the support. Several recent examples of the methods based on such strategy can be mentioned.

Bimetallic catalysts for hydrorefining were obtained by coprecipitation of sulphides in aqueous solutions under argon¹. Precipitation of transition metal sulphides in nonaqueous solutions is a general method of the preparation of dispersed materials²⁻⁴. It is applicable also to sulphides which cannot be precipitated in aqueous solution like chromium sulphide, zirconium sulphide, etc. Sulphides of nickel and tungsten were kneaded with a peptidized alumina powder, the resulting paste was extruded and heated in nitrogen atmosphere⁵. The obtained catalyst exhibited very good activity in partial dearomatization of petroleum distillates. The second metal of the synergic pair, Co or Ni, was deposited in the form of organometallic compound on already sulphided supported molybdenum or tungsten catalyst⁶⁻⁸. It was claimed that an exceptionally large synergic effect can be achieved in this way. The thio compounds, like ammonium thiomolybdate and ammonium thiotungstate, were often applied for preparation of unsupported⁹⁻¹¹

or supported¹² molybdenum sulphide and tungsten sulphide catalysts. Bisthiometalates of the type $[M'(MS_4)_2]^{n-}$, where $n = 2$ or 3 , $M' = Co$ or Ni , and $M = Mo$ or W , were used as precursors of both supported¹³ and unsupported^{14,15} mixed sulphides. It was assumed that an intimate contact between both metals in the precursor would be preserved also in the resulting catalyst and that it would prevent undesirable reactions with the support.

The hydrotreating remains the main field of application of sulphide catalysts. As for other processes, also methanation on sulphur-resistant catalysts seems to be seriously considered¹⁶⁻²¹. The application of thiourea or ammonium thiocyanate was described for the preparation of supported and unsupported transition metal sulphides for methanation²¹. Metal salts were melt together with thiourea or ammonium thiocyanate in the presence of a carrier or its precursor. Heating in a non-oxidizing atmosphere converted the melt to a solid mass which was calcined in inert atmosphere and passivated with diluted air.

A number of combinations of transition metal sulphides has been tested for synergism between components but data in the accessible literature are relatively limited. They concentrate mostly pairs of the type M-Mo or M-W (M stands for a metal) because Mo or W is considered as a main component in the system and Co or Ni as mere promoters. The metals M tried were: Pt; Pd; Ru; Cr; Co; Ni; Cu; V; Ag; Fe; W; Mg; Ca; Sr; Ba; Zn; Al; Ti; Pb; Sn; Bi; Mn^{22,23}, V; Cr; Mn; Fe; Co; Ni; Cu; Zn²⁴, Co; Ni; Zn²⁵, and Ru; Co; Ni²⁶. The strong synergic effect still seems to be a phenomenon limited to Co-Mo, Ni-Mo, Ni-W, and Co-W pairs. It was unambiguously confirmed not only by unnumerable activity measurements but also by the effect of catalyst composition on the distribution of intermediates in hydrodesulphurization²⁷. The synergism in Fe-Mo system is probably only weak²⁴ and might depend on details of preparation. Some authors have not detected it or found even a negative interaction^{22,23}. The positive effect of Zn in alumina supported molybdenum catalysts is probably connected more with zinc-alumina interaction than with cooperation between sulphides²⁵. It was not observed in unsupported Zn-Mo system²⁴. The positive synergism was reported also for Ru-Mo²⁶ pair but this finding require further verification. The negative synergism in Cu-Mo catalyst seems to be well confirmed²²⁻²⁴.

A high intrinsic activity of cobalt and nickel sulphides^{3,28} led to the suggestion that not Mo or W but Co or Ni are the main species in bimetallic catalysts Co-Mo, Ni-Mo, Co-W, and Ni-W. It was concluded that such mixed catalysts should be held for nickel sulphide supported on thiosalts²⁹ or cobalt sulphide supported on MoS₂ (refs^{26,28}). This view implies that rather the pairs Ni-M or Co-M and not the M-Mo or M-W ones should be investigated for the synergism. The data on pairs of this type are rare. The pairs Co-Nb and Ni-V supported on alumina were tested but no significant effect was found²⁶. A small positive synergism was reported in unsupported Co-Nb system³⁰.

There were two purposes of the present work: (i) to modify and to apply to hydrodesulphurization the "thiourea method", recommended for the preparation of methanation catalysts^{20,21} and (ii) to investigate the occurrence of synergism in some less studied pairs of metal sulphides.

Both the modification of the thiourea method and the choice of studied pairs of sulphides were based on the above-mentioned idea that the main species in hydrodesulphurization catalysts are nickel or cobalt sulphide supported on molybdenum

or tungsten sulphide^{26,28,29}. The sulphidic mass which was ment to serve as support of nickel sulphide was prepared here by thermal decomposition of a paste of oxo salt of metal M, thiourea, elemental sulphur, chelating agent, solvent, and silica gel. This procedure differed from the original thiourea method by the addition of sulphur, chelating agent, and organic solvent. Not only classical components Mo or W but also V, Cr, Mn, and Nb were used as the metal M. Thus the special feature of the present work was that the set of studied catalysts was Ni-M while previous authors looking for synergism investigated mostly M-Mo series of sulphides²²⁻²⁶. Nickel was supported here from methanol solution of non-oxidizing salt (nickel acetate) and the final step of preparation was sulphidation by H₂S/H₂ mixture.

EXPERIMENTAL

Preparation of catalysts. The following chemicals were used (crystal water omitted): silica gel CAB-O-Sil M-5, surface area 230 m² g⁻¹ (BDH), MnSO₄, Cr₂(SO₄)₃, (NH₄)₆Mo₇O₂₄, (NH₄)₁₀H₂(W₂O₇)₆, Ni(CH₃COO)₂, Nb₂O₅, V₂O₅, glycerol, sublimated elemental sulphur, thiourea, isopropanol.

Metal salt or oxide, respectively, containing 4.2 mmol of metal was ground in a mortar with 1.8 g of thiourea to fine powder form. A paste of 4.4 g of silica gel in isopropanol, 1 ml of glycerol, and 0.4 g of sulphur were added and the mixture was kneaded for 1 h. The product stood overnight in fume chamber (a part of isopropanol volatilized out) and was thermally decomposed in a stream of nitrogen (200 ml (STP) min⁻¹). It was placed in a boat into a horizontal glass tube which was heated in an oven. The temperature programme applied in decomposition was 10 min at 150°C, 10 min at 250°C, 30 min at 350°C, and 120 min at 400°C. The tube was cooled under nitrogen to ambient temperature, removed from the oven and its inlet and outlet (i.d. 4 mm) were closed by a wool plugs. The slow overnight diffusion of atmospheric oxygen through the plugs passivated the catalysts which were otherwise strongly pyrophoric. The mass obtained was crushed to the 0.16-0.35 mm particles fraction. The resulting catalysts were designated as V-S_x/SiO₂, Nb-S_x/SiO₂, Cr-S_x/SiO₂, Mn-S_x/SiO₂, Mo-S_x/SiO₂, W-S_x/SiO₂, and Ni-S_x/SiO₂. One part of each sample was *ex situ* sulphided and used for catalytic test, the other part of it was used for preparation of the Ni-metal-S_x/SiO₂ catalyst.

A slurry of monometallic catalyst with the appropriate amount of the solution of nickel acetate in methanol (concentration 1.7 g of nickel acetate per 100 ml of methanol) was prepared. After two days of standing it was dried in a vacuum rotary evaporator at 50°C. The obtained catalysts were designated Ni-V-S_x/SiO₂, Ni-Nb-S_x/SiO₂, Ni-Cr-S_x/SiO₂, Ni-Mn-S_x/SiO₂, Ni-Mo-S_x/SiO₂, Ni-W-S_x/SiO₂, and Ni-Ni-S_x/SiO₂. They were *ex situ* presulphidated and used for catalytic and XPS measurements.

The calculated composition of the catalysts was 95 mmol of metal M per 100 g of silica gel for M-S_x/SiO₂ samples and 95 mmol of nickel and 95 mmol of metal M per 100 g of silica gel for Ni-M-S_x/SiO₂ samples. It approximately corresponds to 12 wt. % of MoO₃ for Mo-S_x/SiO₂ and 12 wt. % of MoO₃ and 6 wt. % of NiO for Ni-Mo-S_x/SiO₂, which is a composition comparable to commercial supported catalysts.

Ex situ sulphidation was performed by the mixture H₂S-H₂ (1 : 10) for 2 h at 450°C. The samples were passivated after sulphidation by the same procedure as described above for M-S_x/SiO₂ mass and were stored in air. All samples were and remained almost black with the exception of Ni-S_x/SiO₂ and Ni-Ni-S_x/SiO₂ samples which became gradually grey.

Standard catalysts. Two alumina supported Co-Mo-S_x catalysts were included to activity tests in order to compare the activity of the studied catalysts with industrial catalysts. The first catalyst was commercial product Cherox 3601 manufactured by Chemical Works in Litvínov, Czechoslovakia. The tablets were crushed and sieved to 0.16–0.35 mm particle size fraction. The second catalyst (further designated as NPL) was a sample of the Working Party on Catalyst Reference Materials^{31,32}. The sample was provided as 0.25–0.45 mm particles by National Physical Laboratory, Teddington, Middlesex TW 11, OLW, Great Britain. Both catalysts were presulphided *ex situ* by the same procedure as described above for other samples. Their surface area after sulphidation was 143 and 214 m² g⁻¹, respectively.

Evaluation of catalytic activity. Tubular pressure reactor (i.d. 4 mm) with a fixed catalyst bed was used. The feed was a model mixture of composition decane 85, benzothiophene 3, toluene 10, and durene 2 mol. %. The catalyst charge was 0.3 g, feed rate 15.2 ml (liquid) h⁻¹, flow of hydrogen 6.6 l (STP) h⁻¹, total pressure 2.0 MPa, and temperature 300°C. The liquid products were condensed at -20°C; the samples were withdrawn in 10 min intervals and were analyzed by gas chromatography (3.5 m column packed with 5% Carbowax 20 M on Chromosorb, temperature 200°C, and flow of hydrogen 15 ml min⁻¹). The definition of conversions: Overall conversion of benzothiophene to dihydrobenzothiophene and ethylbenzene $x(\text{BT}) = (n^0(\text{BT}) - n(\text{BT}))/n^0(\text{BT})$, conversion of benzothiophene to dihydrobenzothiophene $x(\text{DHBT}) = n(\text{DHBT})/n^0(\text{BT})$, where n^0 and n are initial and final number of moles, respectively, BT is benzothiophene and DHBT is dihydrobenzothiophene. The temperature of the catalyst in the reactor was increased in the flow of hydrogen at pressure 1.0 MPa during 1 h to 270°C and then the feeding of the liquid was started. The pressure and temperature were adjusted to 2 MPa and 300°C, respectively, and the conversion was followed for 2 h. Only negligible decrease of activity was found during that time and the final conversions are reported here. No significant hydrogenation of aromatic hydrocarbons in the feed was observed in any experiment.

Surface area was measured by adsorption of nitrogen by the chromatographic technique³³ with the mixture hydrogen : nitrogen = 7 : 3. The catalysts were dried before the measurement in the stream of this mixture for 15 min at 165°C.

XPS measurements. X-ray photoelectron spectra of bimetallic catalysts (with the exception of Ni-Nb one) were measured on ESCA 3MK II VG Scientific apparatus using radiation energy corresponding to the line Al K_{α1,2}. The following lines were measured: V 2s, Cr 2p, Mn 2p, Mo 3p, W 4d, Ni 2p, Si 2p, and S 2p. The positions of the lines were corrected on charging effect supposing the bonding energy of Si 2s electrons in SiO₂ to be equal to 153.4 eV (ref.³⁴). The experimental data were analyzed using computation procedure (fitting of the spectrum by a linear background and Gaussian functions) which provided line positions and intensities. Evaluation of element concentration was based on the approximative formula³⁴ $I \approx cE_k^{-1/2}q$, where I is the line intensity, c the surface concentration of emitting atoms, E_k the kinetic energy of electrons of the line measured, and q is the photoionization cross-section³⁵.

RESULTS AND DISCUSSION

Surface areas of the prepared catalysts are presented in Table I. The values for the M-S_x/SiO₂ samples were considerably lower than that of starting silica gel (230 m² g⁻¹). This indicates that a strong interaction of the support with other compounds used in preparation caused a substantial transformation of its texture. The deposition of nickel and subsequent *ex situ* sulphidation resulted in all cases in further small decrease of surface area.

The results of catalytic tests are shown in Table I. The order of activity of the monometallic $M-S_x/SiO_2$ catalysts conforms, with the exception of the $Ni-S_x/SiO_2$ sample, to results of previous comparative studies^{3,22,23,36}. Molybdenum was more active than tungsten and manganese exhibited very low activity. The sample $Ni-S_x/SiO_2$ showed surprisingly poor efficiency. Previous authors found on carbon supported³⁷ and unsupported³ catalysts that the activity of nickel sulphide was in the same range as that of molybdenum and tungsten sulphides.

Table I also shows that the synergic effect in $Ni-M-S_x/SiO_2$ catalysts was unambiguously observed only in the classical pairs $Ni-Mo$ and $Ni-W$. The increase in activity after nickel deposition on the samples with $M = V, Cr,$ and Mn was not higher than the difference between $Ni-S_x/SiO_2$ and $Ni-Ni-S_x/SiO_2$ catalysts; a decrease of the activity was observed for $M = Nb$. Any distinct synergic effect in the pairs $Ni-V, Ni-Cr, Ni-Mn,$ and $Ni-Nb$ was not observed even when the data were corrected for a decrease of surface area after deposition of nickel. This finding agrees with the previous literature which does not report on synergism in the pair $Ni-V$ prepared by an other method²⁶. A solitary result claiming positive synergism in unsupported $Co-Nb$ sulphide³⁰ was not confirmed here by the measurement on the $Ni-Nb$ catalyst.

TABLE I
Catalytic activity and surface area of catalysts

Catalyst	Conversion, %		Surface area $m^2 g^{-1}$
	$x(BT)$	$x(DHBT)$	
$V-S_x/SiO_2$	5.8	1.7	100
$Ni-V-S_x/SiO_2$	11.2	4.8	85
$Cr-S_x/SiO_2$	4.2	1.4	115
$Ni-Cr-S_x/SiO_2$	8.5	3.4	87
$Mn-S_x/SiO_2$	2.6	1.0	92
$Ni-Mn-S_x/SiO_2$	6.6	3.3	74
$Nb-S_x/SiO_2$	5.1	1.5	93
$Ni-Nb-S_x/SiO_2$	2.4	1.3	83
$Mo-S_x/SiO_2$	36.5	20.6	69
$Ni-Mo-S_x/SiO_2$	73.2	1.2	42
$W-S_x/SiO_2$	10.1	5.5	83
$Ni-W-S_x/SiO_2$	53.1	1.1	69
$Ni-S_x/SiO_2$	1.9	0.7	100
$Ni-Ni-S_x/SiO_2$	11.6	5.9	88

The previous generalized analysis of literature data showed that synergic effect on activity in the pairs Co-Mo, Ni-Mo, Co-W, and Ni-W is accompanied by very pronounced changes in the distribution of intermediates in hydrodesulphurization²⁷. In the case of hydrodesulphurization of benzothiophene, the monometallic (Mo, W, Ni, Co) sulphide catalysts produced much more of dihydrobenzothiophene than the bimetallic (Co-Mo, Ni-Mo, Co-W, Ni-W) ones³⁷. This method of diagnosis of the synergic effect can be also applied to data in Table I. It is seen that the mixing in the pairs Ni-Mo and Ni-W caused a sharp decrease in the formation of dihydrobenzothiophene. This is in full agreement with previous results on carbon- and alumina-supported catalysts prepared by the standard impregnation method³⁷. The effect of mixing in remaining Ni-V, Ni-Cr, Ni-Mn, and Ni-Nb pairs can be evaluated in Fig. 1. The data do not seem to indicate any important change in dihydrobenzothiophene formation after nickel deposition on monometallic catalysts, which again conforms to the absence of synergism in activity.

The efficiency of the used preparation method is evaluated in Table II by comparison with conventional samples. (Lower amounts of catalysts (0.02–0.20 g) were used in order not to exceed 70% conversion $x(\text{BT})$; rate constants were calculated assuming first order kinetics). It is seen that the weight activity of Ni-Mo-S_x/SiO₂ sample is lower, but still in the same rank, than Co-Mo-S_x/Al₂O₃ catalysts prepared by the standard procedure. However, the specific feature of the present method was that it produced low surface area catalysts. The relative rate constants normalized to surface area showed that intrinsic activity of the Ni-Mo-S_x/SiO₂ mass was considerably higher than that of the Co-Mo conventional catalysts. The low surface area indicates a proper texture for the reaction of large molecules and this aspect will be the subject of further study.

The first stage of the present method, the decomposition of thiourea complexes, is a modification of procedure recommended for the preparation of methanation

TABLE II
Comparison of activity of prepared Ni-Mo and Ni-W catalysts with commercial Co-Mo samples

Catalyst	Relative first order rate constant	
	normalized to weight	normalized to surface area
Co-Mo-S _x /Al ₂ O ₃ NPL	1.5	1.0
Co-Mo-S _x /Al ₂ O ₃ (Cherox 3601)	1.0	1.0
Ni-Mo-S _x /SiO ₂	0.6	2.0
Ni-W-S _x /SiO ₂	0.3	0.6

catalysts²¹. The original work does not report either on surface area or on the comparison of activity with conventional catalysts. Consequently, the original and the present modified method cannot be compared in this respect.

The main purpose of XPS measurements was to compare the state of nickel combined with various metals in the Ni-M-S_x/SiO₂ samples. However, before coming to these results, some other features in the spectra will be briefly discussed.

The surface composition of samples provided by XPS is presented in Table III. The relative atomic concentration of Ni (related to Si content; $c(\text{Si}) = 100$) was always much lower than 5.7 calculated for the bulk composition (11.4 for Ni-Ni-S_x/SiO₂). This is surprising because nickel was deposited by impregnation of M-S_x/SiO₂ mass and it was expected that this will lead to high surface concentration and fine dispersion of it. The observed data can be understood in two ways. Either nickel sulphide is sintered on the surface to large particles, the bulk of which is not detected by XPS, or the final presulphidation in H₂S/H₂ mixture at 450°C causes a substantial diffusion of nickel into the bulk of the catalyst mass. This conclusion is essentially valid also for all other metals (detected probably as Mo⁴⁺, W⁴⁺, V³⁺, Mn²⁺, Cr³⁺) even when the difference between the relative surface concentrations and the calculated bulk ones (5.7) are not so high as with Ni.

The predominant part of surface sulphur in samples was according to XPS data oxidized to SO₄²⁻ anions (binding energy of S 2p electrons was about 168.2 eV in all samples which conforms to literature data^{34,38}). The presence of S²⁻ (binding

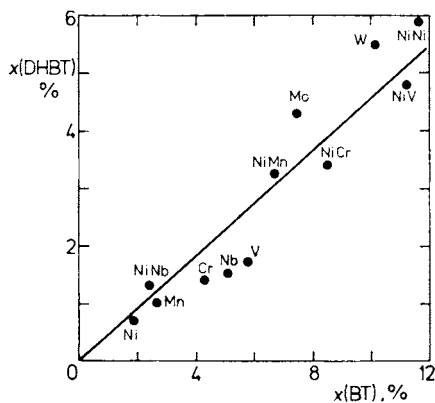


FIG. 1

Comparison of dihydrobenzothiophene formation on various catalysts (the point for Mo was obtained with 50 mg of the catalyst)

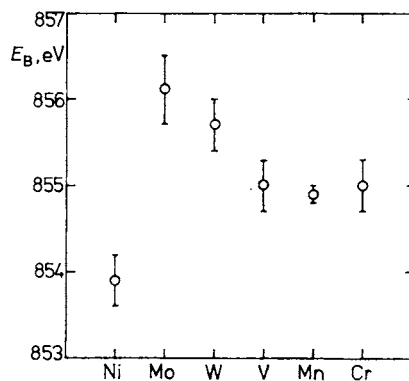


FIG. 2

Binding energies ($2p_{3/2}$) of nickel species in Ni-M-S_x/SiO₂ catalysts (the line segments show the error of measurement, the pair Ni-Nb was not measured)

energy 162.0 eV, refs^{34,38}) cannot be entirely excluded because its detection was less sensitive due to the neighbourhood of very large Si 2*p* peak (153.4 eV). However, the amount of S²⁻ was unambiguously much lower than that of SO₄²⁻. The molar ratio SO₄²⁻/(SO₄²⁻ + S²⁻) for conventional industrial Ni-Mo/Al₂O₃ catalysts treated in the same way as here was in the range from 0.2 to 0.6 (ref.³⁹). This shows that the present Ni-M-S_x/SiO₂ preparations were much more sensitive to air oxidation.

The Ni 2*p*_{3/2} line in all the measured samples showed shake up satellite line shifted by 5.4 ± 1.0 eV from the mother line. The satellite amounts 62 ± 12% of the total line intensity. This effect signifies a 2+ oxidation state of Ni (ref.³⁴). This binding energies (*E*_B) of Ni 2*p*_{3/2} electrons in Ni-M-S_x/SiO₂ samples are compared in Fig. 2. Their values are not suitable for the unambiguous identification of the form of Ni compound present because the tabulated differences in *E*_B of various Ni compounds are relatively small (*E*_B(NiSO₄) - *E*_B(Ni⁰) = 2.3 eV, *E*_B(NiO) - *E*_B(NiS) = 0 eV, *E*_B(NiS) - *E*_B(Ni⁰) = 1.8 eV, ref.³⁴). However, because almost all sulphur was found to be in the form of SO₄²⁻, it can be concluded that all Ni was surrounded mostly by oxygen species. Fig. 2 shows that the *E*_B of Ni is significantly increased by the interaction with the second metal M in the Ni-M-S_x/SiO₂ catalysts.

The increase in *E*_B of Ni accompanying the mixing with Mo or W in fully sulphided (not exposed to air) silica supported catalysts has been already described in the literature^{7,40}; it amounted about 0.6 eV. Similar increase in *E*_B of Co was also observed for related Co-Mo system⁴¹. This phenomenon was interpreted as the result of electron transfer from Ni or Co to Mo or W, and it was suggested that it has a direct relation to the synergic effect⁷. Recent quantum chemical calculations on a set of M'MoS₉ⁿ⁻ clusters, where M' = V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, are in

TABLE III

Relative surface atomic concentrations (related to Si content; *c*(Si) = 100) of Ni-M-S_x/SiO₂ catalysts estimated by XPS

Catalyst M	Component		
	Ni	S	M
Ni	3.8 ± 0.5	4.4 ± 0.9	3.8 ± 0.5
Mo	0.7 ± 0.3	4.2 ± 1.2	2.4 ± 0.8
W	0.6 ± 0.2	3.5 ± 1.0	2.2 ± 0.2
V	1.0 ± 0.3	2.8 ± 1.1	0.5 ± 0.6
Mn	3.2 ± 0.3	4.2 ± 1.3	4.0 ± 1.6
Cr	2.0 ± 0.5	2.3 ± 0.9	3.9 ± 0.7

agreement with these ideas²⁴. It was found, that a significant electron transfer from M to Mo occurs only for Co or Ni. For other metal M', either negligible (V, Cr, Mn, Fe) or opposite (Cu) electron transfer was calculated.

The present work tested the above hypothesis from the other side. The electron transfer between partners in the mixed catalysts measured by XPS was compared not in a set of M–Mo pairs but in the series of Ni–M catalysts. It appeared that the increase of E_B of Ni was a phenomenon not limited to the combinations Ni–Mo and Ni–W but it occurred also in the Ni–Cr, Ni–V, and Ni–Mn samples. It must be admitted that the shift is the highest in the synergic combinations Ni–Mo and Ni–W but it is still of the same order in the nonsynergic pairs. It is concluded that the synergic phenomenon cannot originate only from electron transfer from Ni or Co to Mo or W as suggested by the above interpretation.

CONCLUSION

The studied unconventional method of preparation of hydrodesulphurization catalysts provided Ni–Mo– S_x /SiO₂ sample which had the activity in the same rank as the Co–Mo– S_x /Al₂O₃ catalysts prepared by standard procedures. The Ni–W– S_x /SiO₂ catalyst was also considerably active. The samples containing Ni–V, Ni–Cr, Ni–Mn, and Ni–Nb exhibited low activity and no synergic effect on activity. The absence of synergic effect was further confirmed also by selectivity data on formation of dihydrobenzothiophene in hydrodesulphurization of benzothiophene. The electron transfer from Ni to M in the mixed Ni–M– S_x /SiO₂ catalysts occurred according to XPS measurement not only in the Ni–Mo and Ni–W pairs but (in lesser extent) also in the Ni–Cr, Ni–V, and Ni–Mn pairs. It is therefore not possible to explain simply the synergism in Ni–Mo and Ni–W systems by this electron transfer.

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