MECHANISMS
OF CATALYTIC REACTIONS

The Effect of Nickel on the Component State and HDS Activity of Alumina-supported Heteropolytungstates[1]

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Abstract—Hydrotreating Ni heteropolytungstate catalysts have been prepared by impregnation of γ-Al_2O_3-alumina with solutions of $H_3PW_{12}O_{40}$ acid and its Ni salt. The nickel content is varied by adding $Ni(NO_3)_2$ salt. The calcined samples are characterized by BET, IR, TPR, and XPS techniques. The catalytic activity is tested for HDS of thiophene. It is shown that the initial heteropolyanion, its lacunary analog, and nickel substituted heteropolyanion are present on the surface as a result of the interaction between the active component and the alumina support. The mixed NiWS phase formed after sulfidation determines the HDS activity of the catalysts.

1. INTRODUCTION

Tungsten-containing catalysts are used extensively in important hydrotreating processes including hydrodesulfurization (HDS) of oils. These processes play an essential role in the production of environmentally friendly fuels. Strict environmental regulations stimulate the development of more active catalysts. The most popular catalysts for hydrotreatment processes are Co(Ni)–Mo(W)–based compounds, and that is the reason for their extensive study in the past decade [1].

Recently, an alternative of the hydrotreating catalyst preparation was applied consisting of synthesis from heteropolycompounds [2–4]. There are reports related to the preparation of the hydrodesulfurization (HDS) catalysts using heteropolytungstates [5–8]. The most common compounds used as a support include silica [9, 10], mesoporous silica [11], carbon [12], and to a lesser extent alumina [13]. The use of Mo(W) heteropolyoxometalates as precursors in hydrodesulfurization catalysts is interesting since they present a regular order that allows matching of different metallic elements [14, 15].

The effect of nickel on the HDS activity of catalyst prepared using tungstophosphoric acid (TPA) demands special attention because nickel is known as the best promoter in the W-containing hydrotreating catalysts. In the literature, there are few reports about the nature of oxide precursors of active components in the alumina-supported heteropolytungsten catalysts promoted with Ni [5]. It is interesting to study also the interaction between the loaded components and the support as a function of the preparation method.

In this paper, the influence of nickel quantity on the HDS activity of alumina-supported NiW catalysts has been studied.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The catalysts have been prepared by impregnation of alumina (γ-Al_2O_3 ($S_{BET} \approx 200$ m^2/g) using aqueous solution of TPA and its Ni salt obtained by the method of Tsigdinos [16]. Those are denoted as HPW and NiPW, respectively. The Ni content was varied by using a solution of nickel nitrate. It is loaded on the support before the principal component. For comparison, a sample containing only nickel (2.5 wt % Ni) was also prepared. All catalysts were dried at 120°C and calcined at 400°C for 2 h.

The amount of W in each sample is about 19 wt %, and the nickel content is in the range 0.8–4.4 wt %. The catalysts are listed in Table 1.

2.2. Characterization of the Catalysts

The samples are characterized by BET, IR, TPR, and XPS techniques.

The BET surface area of the catalysts was determined by measuring the adsorption–desorption isotherms of nitrogen at 78 K.

IR spectra (600–1200 cm^{-1}) were recorded on a Bruker IFS-25 Fourier transform IR spectrometer. The samples were pressed with KBr in the ratio 1 : 150. Alumina absorption in the 600–1000 cm^{-1} range was compensated by subtraction of a normalized spectrum

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[1] This article was submitted by the authors in English.

Table 1. Composition and surface area of the catalysts

Sample	Total amount of Ni wt %	Ni/(Ni + W)	S_{BET}, m²/g
γ-Al₂O₃	–	–	200
2.5Ni	2.5	–	185
HPW	–	–	155
NiPW*	0.8	0.12	135
0.4NiNiPW**	1.2	0.17	130
1.7NiNiPW**	2.5	0.28	125
3.6NiNiPW**	4.4	0.41	130

Notes: * NiPW is for nickel salt of tungstophosphoric acid, containing 0.8 wt % Ni.

** 0.4, 1.7, 3.6 wt % Ni are loaded from Ni(NO₃)₂ solution before NiPW salt.

of the equivalent amount of support from the spectra of the catalysts.

In the TPR experiments, a H₂–N₂ mixture (10 vol % H₂) was used to reduce catalysts at a 50 cm³/min flow rate. The temperature was linearly increased (deg/min) up to 850°C.

The XPS measurements were carried out in the analysis chamber of the electron spectrometer ESCALAB-Mkll (VG Scientific). The spectra were excited with unmonochromatized MgK_α radiation at a total instrumental resolution of ~1.0 eV. The binding energies were determined with an accuracy of ±0.1 eV. All binding energies were determined by using the Al 2p photoelectron line centered at 74.8 eV as a reference.

In order to obtain information on the surface composition and the dispersion of the active phases, the atomic ratios were evaluated from the normalized photoelectron intensities. Sulfidation of the samples before XPS measurement was performed in H₂S flow at 400°C for 30 min, then the temperature was lowered to 350°C and maintained for 30 min. After sulfidation, the reactor was cooled down to room temperature under H₂S and transported to the XPS apparatus.

2.3. Catalytic Activity Measurements

The catalytic activity in the HDS reaction of thiophene was measured in a continuous flow reactor system at atmospheric pressure and 350°C. Each experiment was done with a fresh catalyst that was standardized by in-situ calcination in argon up to 400°C. The calcined catalyst was activated by sulfidation with H₂S for 30 min at temperature 400°C and flow rate 40 cm³/min. Then the samples were cooled down in H₂S flow to the reaction temperature of 350°C (30 min). After activation of the catalyst was completed, the catalyst was flushed (30 min) with argon at the same temperature. Reaction products were analyzed using gas chromatograph equipped with a thermal conductivity detec-

tor. Thiophene conversion to C₄ hydrocarbons was taken as a measure of HDS activity. Selectivity of the catalysts, i.e., their ability to hydrogenate created butenes, was calculated as the butane/ΣC₄ hydrocarbons molar ratios.

3. RESULTS AND DISCUSSION

All catalysts under study are listed in Table 1 with their specific surface areas and loaded nickel content.

3.1. BET Surface Area

Impregnation of the alumina with nickel nitrate solution decreases the surface area (~200 m²/g) by ~10% (cf. 2.5Ni sample), while loading with H₃PW₁₂O₄₀ (the HPW sample) and its nickel salt (sample NiPW) (19.5 wt % W) reduces the specific surface area 20–25%. This is an indication that pore-plugging takes place due to the different oxide structures formed with W–O–Al and Ni–W–O bonds. The preliminary loading of the samples with nickel does not decrease their specific surface area within the accuracy of the BET measurements (±5%).

3.2. IR Spectra

In the IR spectrum of the heteropolycompound H₃PW₁₂O₄₀ (Fig. 1), the bands characteristic of a Keggin type structure are observed at 1080 cm⁻¹ (P–O_a), 982 cm⁻¹ (W=O_t), 890 cm⁻¹ (W–O_b–W), and 796 cm⁻¹ (W–O_c–W). Two bands with lower intensity are observed at 598 and 525 cm⁻¹.

The intensities of all these bands decrease in the spectra of catalysts, this being accompanied with the appearance of new features. The assignment of these new bands is difficult because of the overlapping. The shifting of the bands to lower frequencies is a result of the interaction with the support and the partial disordering of the Keggin type structure [10, 13]. The stretching vibration of the P–O_a bond at 1080 cm⁻¹ in the initial anion shifts to higher frequencies in the HPW sample, and a new band appears at 1103 cm⁻¹. The broadening of this band (1020–1140 cm⁻¹) leads to overlapping with the new feature at 1103 cm⁻¹ characteristic for lacunary anion [PW₁₁O₃₉]⁷⁻ and Al(Ni) phosphates [17].

In the spectrum of the NiPW sample, the bands at 1080 and 982 cm⁻¹ are shifted to lower frequencies, i.e., 1072 and 965 cm⁻¹, respectively. No substantial change in the frequencies of the W–O_b–W bond at 880 cm⁻¹ is an indication for a partial conservation of the Keggin type structure although some part of the anion is destroyed as a result of the interaction with the support. The band characteristic of the W–O_c–W bond is shifted to higher frequencies (824 cm⁻¹), and new bands in the region 750–650 cm⁻¹ appear. The lacunary anion is formed as a result of the partial hydrolysis of the initial anion (pH of the suspension is about 5.5–6.0):
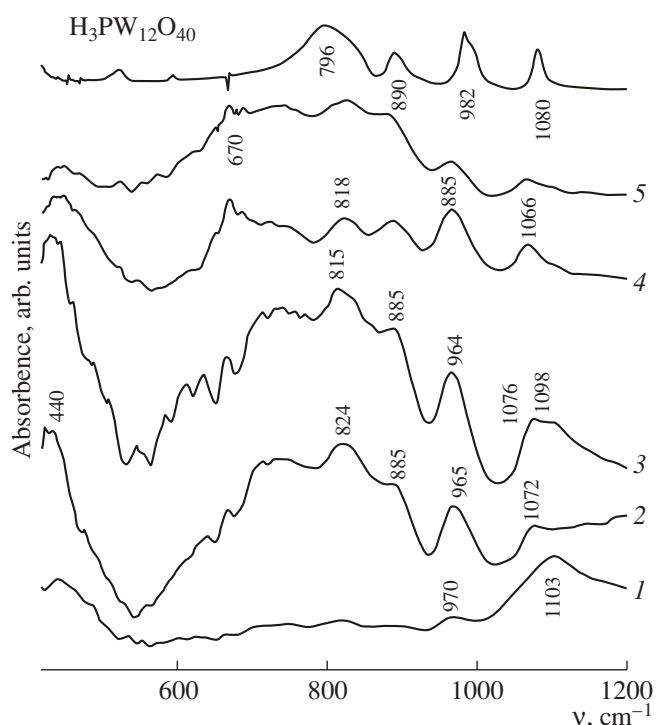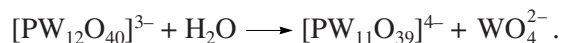
Fig. 1. IR spectra of alumina-supported catalysts calcined at 400°C. (*1*) HPW, (*2*) NiPW, (*3*) 0.4NiNiPW, (*4*) 1.7NiNiPW, (*5*) 3.6NiNiPW.

Fig. 2. TPR profiles of pure $H_3PW_{12}O_{40}$ acid and Ni heteropolytungsten catalysts.

$$[PW_{12}O_{40}]^{3-} + H_2O \longrightarrow [PW_{11}O_{39}]^{4-} + WO_4^{2-}.$$

In all catalysts a new band at about 440 cm^{-1} is observed. Its intensity is related to the nickel included in the samples and depends on the amount and the method of nickel loading (nickel salt of the heteropolyacid or nickel loaded additionally).

The presence of this band in the spectra of all samples confirms the formation of a polymeric structure [18]. Possibly, in nickel-containing samples, polymeric compounds are formed with W–O–Ni bonds. Perturbation in the bands of the bridge bonds of the heteropolycompounds suggests Ni inclusion in the W surrounding and the W–O–Ni bond formation [19]. The band at about 440 cm^{-1} is changed with Ni loading. This band is characteristic of the Ni–O bond [20] but is also observed in the IR spectrum of $[W_6O_{19}]^{2-}$ anions [18]. Therefore, we assign this feature to the formation of W–O–Ni and W–O–W bonds in polymeric compounds and also to a distinct NiO phase.

3.3. TPR

The TPR profiles of pure $H_3PW_{12}O_{40}$ acid and Ni heteropolytungsten catalysts are shown in Fig. 2. For the initial $H_3PW_{12}O_{40}$ acid, two maxima are observed. The first one at 470°C is related to the loss of the framework oxygen by the acid molecule before its decomposition [21]. The next feature appearing at temperatures above 600°C is an indication of the WO$_3$ oxide reduc-

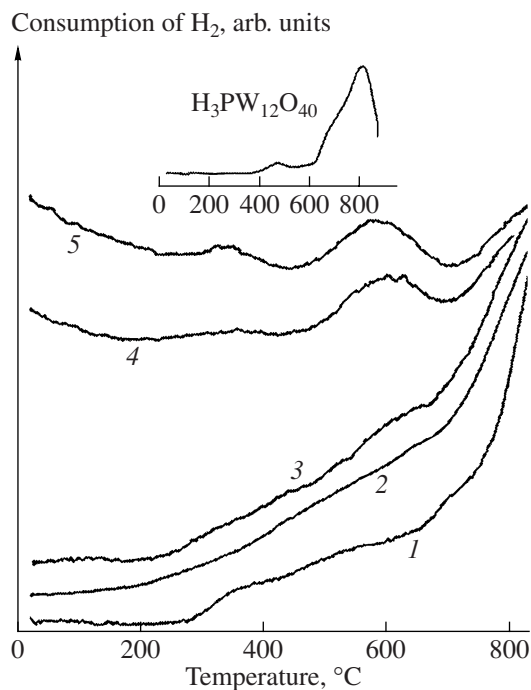tion. TPR profiles of all samples show heterogeneity of the phase composition. In the TPR profile of supported heteropolyacid (HPW sample), the first peak appears at lower temperature, i.e., ~350°C (instead of 470°C for pure $H_3PW_{12}O_{40}$ acid). This result confirms the polymeric compound formation, which is reduced at lower temperatures.

The onset of reduction for nickel-containing catalysts begins also at lower temperatures. The TPR profile of the NiPW sample goes steeply starting at temperatures as low as ~200°C, and a peak is formed at around ~600°C for 0.4 wt % preliminary introduced nickel. In accordance with IR results, this peak reflects the reduction of the $[PW_{11}NiO_{39}]^{5-}$ heteropolyanion. The intensity of this peak increases with the nickel content (curves *4*, *5*). T_{max} is shifted to a lower temperature as compared to the case of the 0.4NiNiPW sample. The low temperature peak at 320°C appears at the highest Ni content (curve *5*) and is related to the reduction of the highly dispersed NiO particles. The peaks at temperatures above 800°C reflect tungsten-containing species modified due to the interaction with the support (Fig. 2).

3.4. XPS Analysis

The W $4f_{7/2}$ peak with binding energy of 36.3 eV in the XPS spectrum of the catalysts in the oxide form (Fig. 3) is characteristic of W in the oxidation state +6 [22, 23]. The XPS spectra of tungstophosphoric acid

Intensity, arb. units
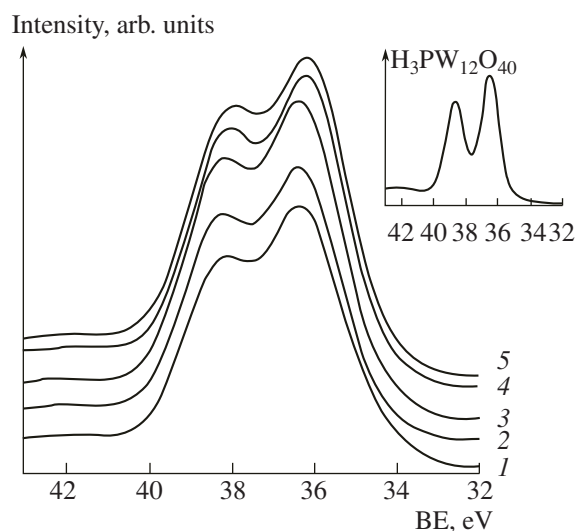
Fig. 3. W $4f$ line of $H_3PW_{12}O_{40}$ acid and supported heteropolytungsten catalysts calcined in air. (*1*) HPW, (*2*) NiPW, (*3*) 0.4NiNiPW, (*4*) 1.7NiNiPW, (*5*) 3.6NiNiPW.

Intensity, arb. units
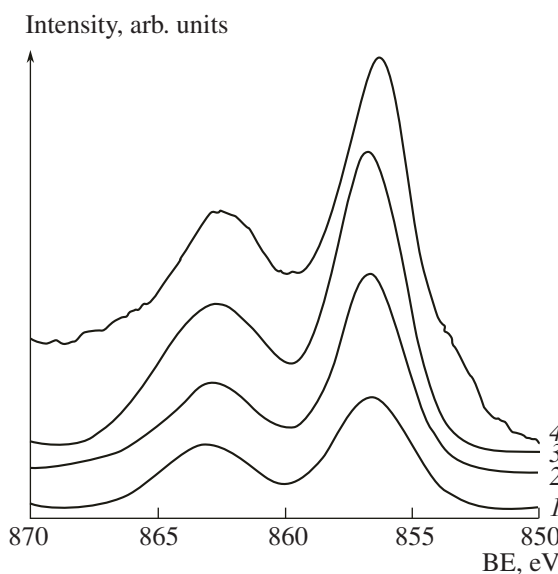
Fig. 4. Ni $2p_{3/2}$ line of Ni heteropolytungsten catalysts calcined in air. (*1*) NiPW, (*2*) 0.4NiNiPW, (*3*) 1.7NiNiPW, (*4*) 3.6NiNiPW.

impregnated on γ-Al_2O_3 and Ni-containing catalysts reveal a broad, not well resolved doublet as compared to that of pure $H_3PW_{12}O_{40}$. The explanation could be related to the very small thickness of W-containing species covering the high surface area alumina. The BE of the Ni $2p_{3/2}$ line (856.3 eV) in all samples shows the presence of Ni^{2+} ions distributed in a mixed oxide matrix (Fig. 4) [24]. Only in the case of 3.6 wt % Ni (3.6NiNiPW sample) is a shoulder with a lower binding energy of 854.2 eV observed. It is related to the presence of small NiO particles.

The binding energy of the P $2p$ line at 135.0 eV is assigned to phosphorus in phosphates [25].

The XPS-derived surface composition (Table 2) indicates nickel preservation on the surface of the catalysts with tungsten being in similar quantities for all samples. These data suggest that nickel stabilizes the heteropolyanion on the surface $[PW_{11}O_{39}]^{7-}$, and this assumption is also confirmed by the IR data [26].

After sulfidation of the samples, the W $4f$ line has a complex structure and can be represented by three doublets with binding energies for W $4f_{7/2}$—31.2, 32.5–33.0, and 36.3 eV corresponding to WS_2, WO_xS_y, and WO_3, respectively (Fig. 5) [8].

The Ni $2p_{3/2}$ main line at 853.2 eV binding energy (Fig. 6) is assigned to the NiS_x formation. The slight asymmetry towards higher binding energies represents nickel Ni^{2+} ions from the unsulfided part of the catalysts [24].

The binding energy of the P $2p$ line does not change after sulfidation (135.0 eV) and is assigned to phosphorus in PO_4^{2-}.

The S^{2-} ions and/or S_2^{2-} ions with BE of 162.0 eV are present [27]. No intensity was observed at ~169 eV, indicating that no sulfate species are present on the surface; i.e., no oxidation of the catalysts occurred during

Table 2. Surface composition of catalysts (at %) in oxide form (ox.) and after sulfidation (sulf.)

Sample	Ni $2p$		W $4f$		O $1s$		Al $2p$		P $2p$		S $2p$
	ox	sulf	ox	sulf	ox	sulf	ox	sulf	ox	sulf	
2.5Ni	0.2	0.2	–	–	59.7	57.2	39.3	40.7	–	–	1.2
HPW	–	–	2.7	2.6	57.4	51.4	39.3	40.2	0.7	0.6	5.2
NiPW	0.4	0.2	2.4	4.8	58.7	46.3	38.1	37.9	0.5	0.5	10.4
0.4NiNiPW	0.6	0.4	2.8	4.0	58.2	47.6	37.8	38.2	0.6	0.6	9.4
1.7NiNiPW	0.8	0.6	2.8	4.2	58.1	46.7	37.8	36.9	0.5	0.5	11.3
3.6NiNiPW	1.1	0.6	2.9	2.8	58.2	48.9	37.0	38.1	0.7	0.6	9.1
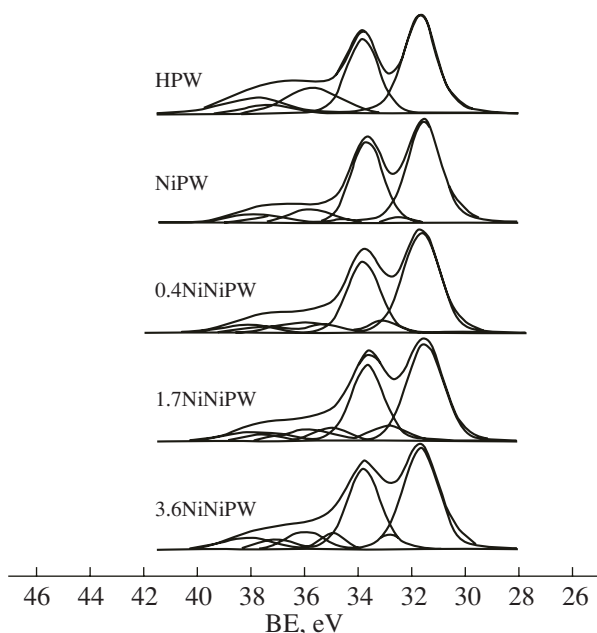
Fig. 5. W 4*f* line of alumina-supported heteropolytungsten catalysts after sulfidation.

Fig. 6. Ni $2p_{3/2}$ line of catalysts after sulfidation.

the transfer of the samples from the reactor to the XPS chamber.

The amount of nickel on the surface for the NiPW sample decreases significantly after sulfidation, whereas the W concentration increases (Table 2). Small amounts of nickel (0.4 wt %) loaded preliminary increase its surface concentration. Probably in this way, the nickel is included into the $[PW_{11}NiO_{39}]^{5-}$ heteropolyanion. No change in the phosphorus concentration is observed.

3.5. Catalytic Activity

The dependence of the steady-state conversion of the catalysts on the atomic ratio Ni/(Ni + W) after sulfidation with H_2S is presented in Fig. 7.

The low activity of the HPW sample increases 2.5 times when the nickel salt of the tungstophosphoric acid is loaded. In the sample NiPW Ni/(Ni + W), the atomic ratio is equal to 0.12. The catalytic activity increases when a small amount of nickel is introduced preliminarily on the support. The strong synergetic effect is revealed when 0.4 wt % Ni is loaded additionally (Ni/(Ni + W) = 0.17) in comparison to the NiPW sample. No noticeable dependence of the hydrogenation activity on the atomic ratio Ni/(Ni + W) is observed.

Figure 8 shows the activity changes with time on the stream. The initial activity of the catalysts is significantly higher as compared to the steady-state conversion regime. It suggests that the phase composition of the heteropolytungstates supported and sulfided with H_2S is altered during the reaction. An exception to this

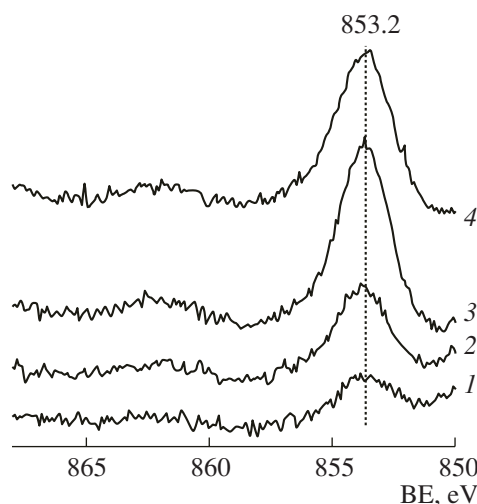is the catalyst with the highest content of nickel loaded preliminarily (the 3.6NiNiPW sample).

Most probably, the initial activity is related to the formation of SH groups during the sulfidation as well as the OH groups that remain on the surface [28]. The SH groups are the result of a dissociative adsorption of H_2S [29]. Oxosulfided tungsten species, NiS_x and WS_2 along with these SH and OH groups, can generate active sites for the thiophene conversion. According to XPS data, the sulfided NiW phase is very important for the formation of active sites and their participation in the steady-state activity.

The higher amount of nickel loaded additionally promotes the establishment of the steady-state activity. This result correlates with the increase of the NiW amount (0.4NiNiPW sample). With the Ni amount loaded additionally (1.7 and 3.6 wt %), nickel forms
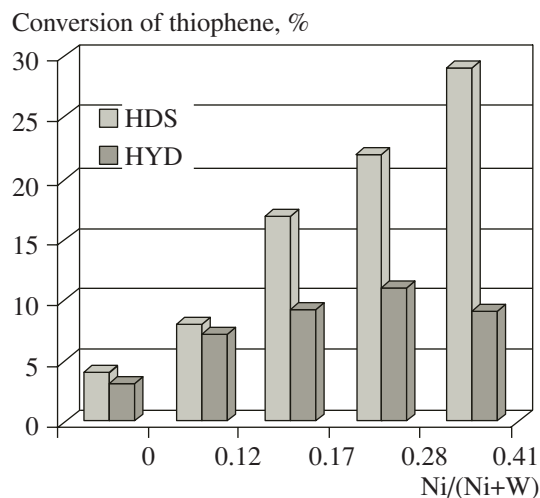

Fig. 7. Steady-state HDS activity and HYD as a function of the Ni/(Ni + W) ratio.
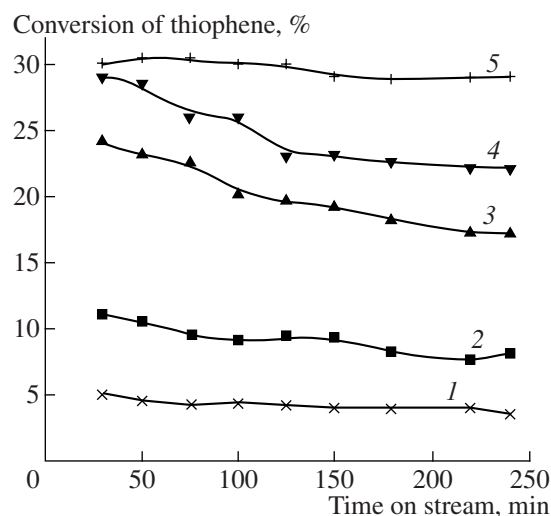
Conversion of thiophene, %

Fig. 8. Evolution of thiophene conversion with time on stream over catalysts.

separate NiS$_x$ particles. An increase and stabilization of the HDS activity is observed as a result of the interplay between NiS$_x$ and WS$_2$ phases, which form an additional amount of the NiWS phase.

XPS data for the 1.7NiNiPW catalyst after prolonged testing shows no change in the surface concentration. The catalyst surface consists of WS$_2$, NiSx, and a small amount of unsulfided W. Most probably, in the studied time on-stream these phases take part in formation of active sites in thiophene hydrodesulfurizaton.

4. CONCLUSIONS

A strong synergetic effect between Ni and W is observed at low Ni concentrations and is related to the formation of mixed NiW oxide compounds being precursors of the active phase.

After sulfidation, the mixed NiWS phase is formed. Its structure and amount is determined by oxide precursors—the newly formed heteropolyanion as well as separated W- and Ni-containing phases.

Preliminary introduction of the 0.4 wt % Ni in the support increases sharply the HDS activity.

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