

Synergism between Ni and W in the NiW/ γ -Al₂O₃ hydrotreating catalysts

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Received 15 June 2005; accepted 24 June 2005

A series of NiW/ γ -Al₂O₃ catalysts (20 and 30 wt% W and 1–5 wt% Ni) have been prepared and studied by TPR and XPS. HDS activity has been tested in the thiophene conversion. The effect of Ni and W loadings on the formation of different structures is presented. In the calcined catalysts several phases coexist, concentrations of which depend on the Ni/(Ni + W) atomic ratio. The Ni synergistic effect in the HDS reaction is confirmed by the increase in the HDS activity (~10–15 times). This effect is ascribed to the formation of an active NiWS phase of high dispersion from the mixed NiW oxide precursors. At higher Ni/Ni + W ratio a redistribution of active components in additional amount of NiWS phase during sulfidation is suggested.

KEY WORDS: NiW/ γ -Al₂O₃; Thiophene hydrodesulfurization; TPR; XPS.

1. Introduction

The hydrotreating processes play an important role in the production of environmentally friendly fuels with lower level of sulfur and nitrogen. Environmental restrictions imposed on the fuels quality, in the USA for example, will limit the level of sulfur content to 15 ppm in 2006. In order to meet these requirements, along with an increase of the pressure and the temperature in the reaction it will be necessary to search for more effective catalysts also. In industry, the most widely used catalysts are Co(Ni)Mo and NiW supported on alumina [1]. Different supports have been studied in the preparation of the catalysts [2–8], but up to now the most widely used one still remains alumina. NiW/ γ -Al₂O₃ catalysts show a higher activity in deep hydrodesulfurization (HDS) and hydrogenation (HYD) of crude oils.

Lately W-containing catalysts have been studied more intensively. In spite of numerous studies, synergistic effect observed between Ni and W in the NiW hydrodesulfurization catalysts remains not fully understood. A correlation between phases formed during the preparation of the catalysts and their catalytic activity is also a matter of debate.

As far as the phase composition of the NiW/ γ -Al₂O₃ catalysts is concerned, the formation of polytungstates, NiWO₄, and nickel aluminate was established [9–14]. The absence of Al₂(WO₄)₃ phase in these catalysts was noted in [9, 15], although Biloen *et al.* [16] did not rule out a solid-state reaction between WO₃ and the support forming some kind of defective Al₂(WO₄)₃-like structure.

Kim *et al.* [10] suggested that NiWO₄ is a precursor for the active phase, while Mangnus *et al.* [12] found that its sulfidation temperature is too high as compared to that of the reaction. According to authors in [11, 12], the precursor is connected with NiWOA1. Promoting effect of Ni is related to the formation of NiWS phase, similarly as the addition of Co to the Mo/ γ -Al₂O₃ catalysts is related to the formation of CoMoS phase [1]. The active NiWS phase is formed during sulfidation from oxide phase precursors [12]. Other authors report that the formation of the active NiWS phase occurs by migration of NiS to the edges of WS₂ slabs, so-called redispersion [2, 3, 17–20]. In contrary the CoS species are expected to be less mobile and do not migrate to form an active CoWS phase [21].

The purpose of the present work is to demonstrate the relation between chemical states of W and Ni on the surface of alumina-supported NiW catalysts in both, calcined and sulfided forms to their reducibility and catalytic activity in thiophene hydrodesulfurization reaction. The effect of Ni and W loading on the phase composition and its relation to activity has been discussed.

2. Experimental

2.1. Catalyst preparation

The alumina-supported catalysts with different W and Ni content were prepared by the incipient wetness method. W and Ni have been impregnated simultaneously on γ -Al₂O₃ (S_{BET} = 200 m²/g) using the aqueous solution of ammonium metatungstate (NH₄)₆H₂W₁₂O₄₀·H₂O and nickel nitrate Ni(NO₃)₂·6H₂O loaded in an

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appropriate ratio. Then, the samples were dried for 4 h at 120 °C and finally calcined for 2 h at 400 °C. The prepared catalysts are denoted by letters Ni and W, with concentrations (in wt%) of the component given in front of the metals abbreviations. The Ni/(Ni + W) atomic ratios range from 0.11 to 0.44. All prepared catalysts are listed in Table 1.

Some standards were also prepared in order to facilitate the determination of different chemical states of Ni and W in the catalysts: NiWO₄ was prepared by calcination (2 h at 900 °C) of nickel nitrate and H₂WO₄ mixture, NiAl₂O₄ was synthesized by dissolution of the Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O salts, evaporation of water, drying at 105 °C and calcination for 2 h at 900 °C.

Heteropolynickelate of Anderson type (NH₄)₄[NiW₆O₂₄H₆]·H₂O was prepared in accordance with [22]. Phase purity of standards was checked by X-ray diffraction.

2.2. Catalysts characterization

TPR experiments were carried out in an apparatus described previously [23]. The H₂-N₂ mixture (10 mole % H₂) was used to reduce catalysts at 50 cm³min⁻¹ flow rate. The temperature was linearly increased up to 850 °C.

The XPS measurements were carried out in the analysis chamber of the electron spectrometer ESCALAB-MkII (VG Scientific) with a base pressure of ~ 10⁻⁸ Pa. The spectra were excited with an unmonochromatized MgK α radiation ($h\nu$ = 1253.6 eV) at total instrumental resolution of ~ 0.9 eV as measured by the FWHM of Ag 3d_{5/2} photoelectron line. The binding energies were determined with accuracy of $\pm$ 0.1 eV. In some cases, especially after sulfidation, a non-uniform surface charging was observed during spectra acquisition. This effect was strongly suppressed by electrical isolation of the sample holder from the ground. All spectra were calibrated by using (whenever possible) Al 2p photoelectron line 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, i.e. peak areas divided by the corresponding photo-ionization cross sections taken from Scofield. Sulfidation of the samples before XPS measurement was performed in H₂S flow (40 cm³ min⁻¹) at 400 °C for 1 h. After sulfidation, the reactor was cooled down to room temperature under H₂S and transported to XPS apparatus under N₂ atmosphere.

2.3. Catalytic activity measurements

The catalytic activity in HDS reaction of thiophene was measured in a continuous flow reactor system connected with a gas chromatograph at atmospheric pressure and 350 °C. Each experiment was done with a fresh catalyst that was standardized by in-situ calcination (60 min) in argon up to 400 °C. The calcined catalyst was activated by sulfidation with H₂S during 1 h at temperature 400 °C and flow rate 40 cm³ min⁻¹. Then the samples were cooled down in H₂S flow to the reaction temperature 350 °C. After the activation of the catalyst had been completed, the catalyst was flushed (30 min) with argon at the same temperature.

The thiophene was introduced into the reactor by flowing H₂ through a thiophene saturator. Activity of the catalyst has been measuring for 5 h. Reaction products were analyzed using gas chromatograph equipped with a thermal conductivity detector. 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/ Σ C₄ hydrocarbons molar ratios.

3. Results and discussion

The composition and some properties of the samples under investigation are presented in Table 1.

3.1. TPR

The TPR profiles (figure 1) of both Ni/ γ -Al₂O₃ catalysts (2.4Ni and 4.2Ni) show two peaks of different

Table 1
Composition, TPR data and HYD (in %) of NiW/ γ -Al₂O₃ catalysts at various Ni and W loadings

Sample	Ni wt%	W wt%	Ni/(Ni + W)	mmolH ₂ /g 20–650 °C	mmolH ₂ /g 20–800 °C	HYD %
2.4Ni	2.4	–	1.00	0.40	0.56	3.0
4.2Ni	4.2	–	1.00	0.59	0.78	3.0
20W	–	19.5	0.00	0.37	0.93	6.0
1Ni20W	1.2	19.5	0.17	0.44	0.99	13.0
3Ni20W	3.0	19.5	0.32	0.82	1.58	15.0
5Ni20W	5.0	19.5	0.44	1.25	2.04	12.0
30W	–	30.0	0.00	0.58	1.55	5.0
1Ni30W	1.2	30.0	0.11	0.79	1.84	7.0
3Ni30W	3.0	30.0	0.24	1.00	2.05	12.0
5Ni30W	4.7	30.0	0.33	1.63	2.73	21.0
NiWO ₄	0.1	0.3	0.5	3.73	10.60	–

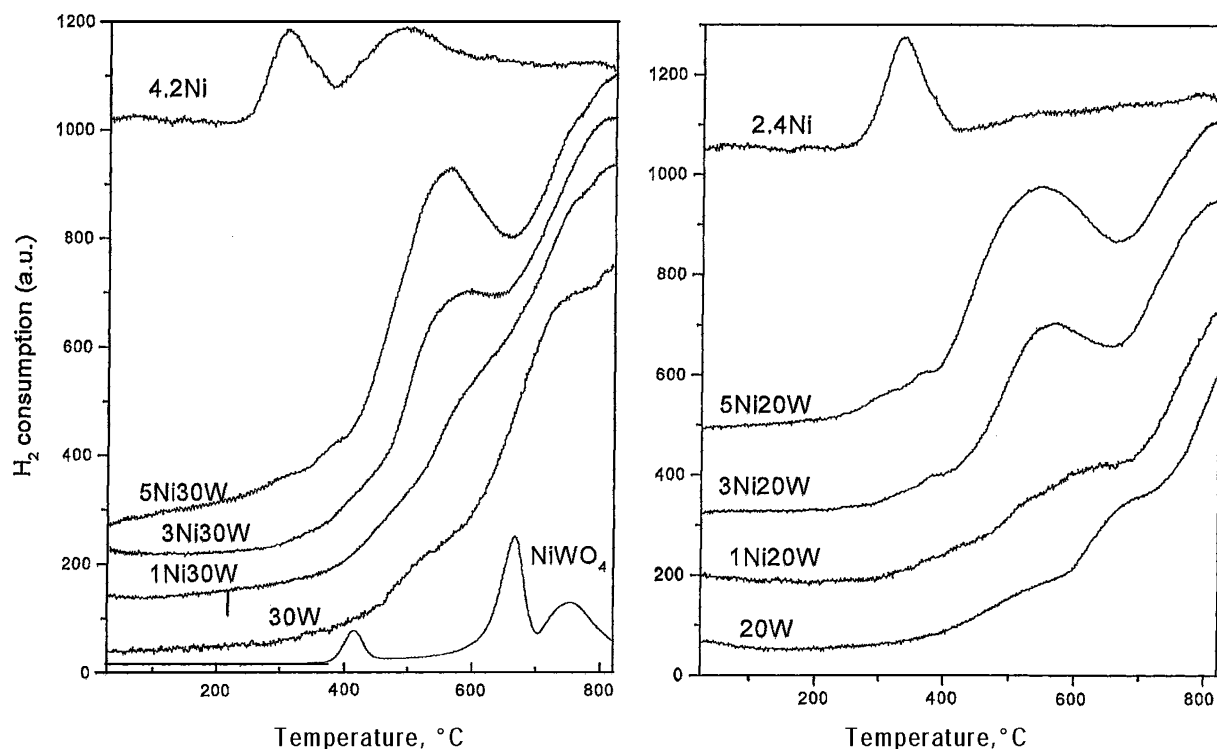


Figure 1. TPR patterns of NiWO_4 and NiW supported alumina catalysts.

intensity. The first peak is centered at $\sim 332^\circ\text{C}$ (2.4Ni catalyst) and at 307°C (4.2Ni catalyst). This peak can be ascribed to the reduction of NiO surface phase [11]. The second peak in the TPR profile for 4.2Ni catalyst is very broad, T_{max} value being $\sim 493^\circ\text{C}$. The width of this peak indicates a poorly defined phase consisting of Ni species in contact with variable amount of Al^{3+} neighbors [12]. These species (and corresponding TPR peak) seem to be present also in the 2.4Ni catalyst but in considerably lower concentration. Peaks of very low intensity are observed in the high-temperature region ($760\text{--}790^\circ\text{C}$) and they can be ascribed to the reduction of NiAl_2O_4 phase [12]. The TPR patterns of the 20 W and 30 W catalysts reveal broad peaks of low intensity with T_{max} at $\sim 550^\circ\text{C}$, 700°C and above 800°C (figure 1). These peaks can be ascribed to the reduction of dispersed W species with different reducibility [10]. Benitez *et al.* [24] reported that octahedrally coordinated WO_x species (probably in polytungstate phase) are reduced at temperatures varying in the $300\text{--}600^\circ\text{C}$ range. The peaks appearing at higher temperatures could be attributed to the reduction of other W-containing phases.

The TPR results for the NiW catalysts reveal the heterogeneous nature of NiW phases formed on the alumina surface in addition to the complicated IR spectra of these structures [25]. The TPR patterns show mutual effect of Ni and W components on the reduction temperature (figure 1): the onset of the reduction for NiW samples (figure 1) shifts towards lower temperatures as compared to $\text{W}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ samples,

especially for NiW with 30 wt% W. It appears that some part of Ni forms a separate, highly dispersed, easy reducible phase. The low-temperature peak (T_{max} around $390\text{--}400^\circ\text{C}$) appears in the TPR patterns with increasing Ni amount. This peak is clearly detected in both catalysts with higher Ni concentrations (5Ni30W and 5Ni20W). We ascribe this peak to reduction of a highly dispersed NiO surface phase [12]. This peak (at 415°C , figure 1) is also presented in the TPR profile of the NiWO_4 which contains a small amount of extra NiO phase as revealed by XRD. The curves form and T_{max} in the region $400\text{--}650^\circ\text{C}$ shows a nickelpolytungstate phase reduction which overlaps with another NiWO_4 like phase which is reduced at slightly higher temperature. The polytungstate phases are reduced at lower temperature than WO_3 [11]. The reduction of NiWO_4 phase along with other W-containing phases starts at temperatures around 600°C . This is confirmed when comparing the TPR profile of NiWO_4 with distinct peak features at 666 and 753°C characteristic for reduction of Ni and W species (figure 1). We can not rule out reduction of NiAl_2O_4 – spinel like structure which is reduced at the high temperature (830°C) according to Kim *et al.* [10].

3.2. XPS analysis

The binding energies of W, Ni and S species are presented in table 2. For comparison, the BE of some standards are also included.

As one can see from table 2, the BE of $\text{W}4f_{7/2}$ for NiW catalysts in the oxide form are the same as those of

Table 2
Binding energies (eV) of the elements of alumina-supported NiW catalysts and standards

Sample	W4f _{7/2}		Ni2p _{3/2}		O1s		Al2p		S2p _{3/2}
	ox	sulf	ox	sulf	ox	sulf	ox	sulfs	
2.4Ni	—	—	856.6	853.0	531.6	531.5	74.8	74.8	161.5
20W	36.3	31.8	—	—	531.4	531.5	74.8	74.8	161.5
1Ni20W	36.3	31.5	856.5	852.9	531.5	531.5	74.8	74.8	161.2
3Ni20W	36.2	31.5	856.4	852.9	531.5	531.5	74.8	74.8	161.2
5Ni20W	36.2	32.1	856.2	853.5	531.4	531.4	74.8	74.8	162.0
1Ni30W	36.2	31.6	856.3	853.3	531.4	531.5	74.8	74.8	161.4
3Ni30W	36.3	31.5	856.6	853.0	531.5	531.4	74.8	74.8	161.2
5Ni30W	36.2	31.6	856.4	853.0	531.4	531.4	74.8	74.8	161.3
Standard									
WO ₃	36.1	—	—	—	530.5	—	—	—	—
WS ₂	—	31.6	—	—	—	—	—	—	161.2
NiWO ₄	36.1	31.9	856.3	853.4	530.8	—	—	—	161.8
Ni _{0.17} W _{1.04} O ₄ ^b	36.0	31.8	856.4	853.6	530.7	—	—	—	161.8
NiAl ₂ O ₄	—	—	856.2	856.4	531.4	531.7	74.8	74.8	161.9
+ 2 wt%NiO	—	—	—	853.4	—	—	—	—	—
NiO	—	—	856.0	853.3	530.0	—	—	—	162.0 ^a
			854.7						

^a In the case of a complex S2p line shape, the lowest binding energy is presented.

^b Ni_{0.17}W_{1.04}O₄ represents atomic concentration obtained from XPS for nickelpolytungstate.

WO₃ and NiWO₄ standards. The W4f photoelectron line decompositions for some of the catalysts after sulfidation are presented in figure 2.

W4f line is reproduced as a sum of two standard spectra. The lower BE standard represents sulfided heteropolynickelate of Anderson type, while the higher BE (calcined component) corresponds to oxide form. All the spectra after sulfidation can be fitted with a W4f doublet with W4f_{7/2} binding energy at 36.2 eV and one at 31.5 eV, corresponding to W⁶⁺-oxide and W⁴⁺-sulfide species [9, 26, 27].

The W⁶⁺ component of the spectra can be related to the presence of the NiWO₄ phase in the catalysts, because polytungstates are sulfided to higher extent. A third doublet with W4f_{7/2} binding energy at 33.0 eV should be noted for 5Ni20W catalyst (Ni/(Ni + W) = 0.44). This doublet can be assigned to oxysulfidic W species or WS₃ according Coulier *et al.* [2]. It is worth to note, that such doublet is not observed in the catalysts with 30 wt% of W (figure 2).

Curve fitting of the W4f photoelectron line allows one to estimate the degree of tungsten sulfidation, which is about 90%. The high degree of sulfidation can be related to the formation of W species of nanometer size. On the contrary, Zuo *et al.* [19] have found no significant change in the sulfidation degree with the Ni content. We explain this difference with no change in the Ni surface concentration during sulfidation.

Figure 3 shows Ni2p spectra of NiW/ γ -Al₂O₃ catalysts calcined at 400 °C. The line shapes for all catalysts are similar. The main peak at 856.3 eV has a low binding energy shoulder at 854.2 eV. The presence of this shoulder can be explained with NiO particles of

bigger size [28] or with a nickel species having different coordination due to the alumina support.

As BE value of the Ni 2p_{3/2} main line is the same as that of in NiAl₂O₄, NiWO₄ and polymeric NiW compounds (table 2) this peak could be ascribed to Ni in all these compounds. The results confirm the DRS and IR spectra data [25] indicating that all nickelpolytungstates, NiWO₄ and NiAl₂O₄- spinel like structure are present in the catalysts and their concentration is governed by the Ni/(Ni + W) ratio. Spectral decomposition of the Ni 2P_{3/2} line in the sulfided catalysts into two components (figure 4) gives a peak with binding energy at 853.0 eV, characteristic for nickel sulfide and another one with BE at 856.3 eV corresponding to oxidic species.

Ni2p line is reproduced as a sum of two standard spectra. The lower BE standard represents sulfided standard heteropolynickelate of Anderson type, while the higher BE (calcined component) is taken from the corresponding oxide components. The Ni2p_{3/2} line positions for sulfided catalysts are very close to that of sulfided NiWO₄ (table 2) and polytungstate phases used as standards. This suggests that Ni in all Ni–W–O structure like polytungstate and NiWO₄ after sulfidation is present in a similar NiWS phase where nickel is in contact with WS₂ [29]. Closest values for W4f_{7/2} and Ni2p_{3/2} to that for sulfided NiWO₄ are observed for 5Ni20W catalysts (Ni/(Ni + W) = 0.44 versus, Ni/(Ni + W) = 0.50 for NiWO₄) which is an indication of a NiWS like phase formation (table 2).

We would like to comment the changes in surface atomic ratios observed after sulfidation (table 3). The W4f/Al 2p ratio for the non-promoted W sample is 0.07 and does not increase after sulfidation confirming sulfi-

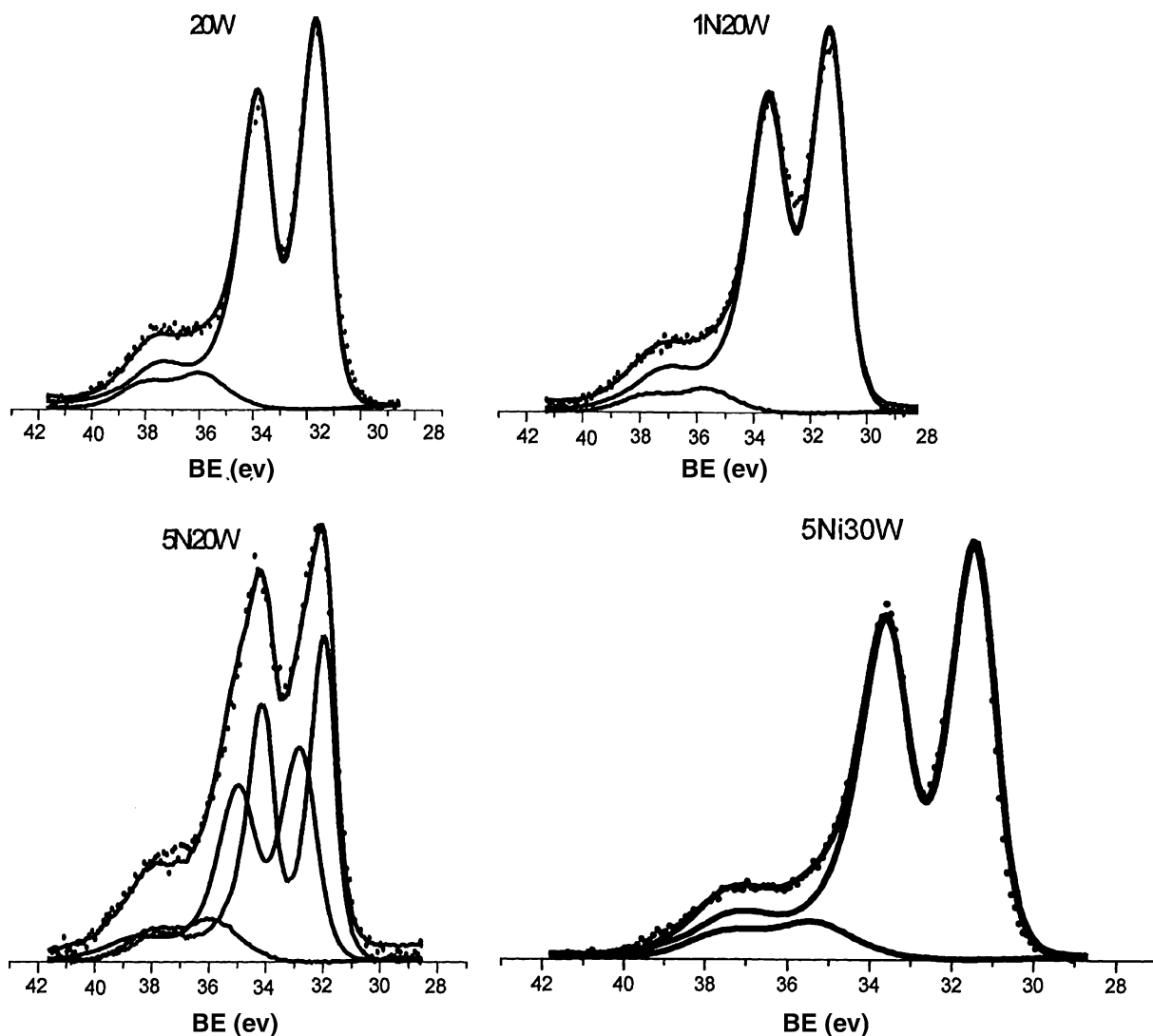


Figure 2. W4f line decomposition after sulfidation at 400 °C.

dation of W without significant changes in its dispersion. An addition of Ni results in a slight increase of W/Al ratio after sulfidation, which can be explained with redistribution of tungsten sulfide over the alumina surface.

The Ni/Al ratios on the surface of the catalysts increase from 0.01 to 0.04 and do not change after sulfidation. Small amounts of Ni clusters are not excluded. Nickel species remain on the surface close to the W species. The surface Ni concentration decreases after sulfidation in the 5Ni20W sample only (no change of W/Al ratio after sulfidation is observed). We could suggest that Ni in this catalyst reacts with oxysulfidic or WS_3 species as revealed in the XPS spectra of this catalyst (figure 2). The elemental sulfur created after sulfidation covers Ni species and thus attenuates the $\text{Ni}2p$ intensity.

The higher surface Ni concentration in the 5Ni30W sample (table 3) correlates with the TPR data (figure 1), which reveals more NiO on the surface. A separate,

highly dispersed NiS phase is formed from NiO particles after sulfidation. One can suppose that NiS phase assists in the formation of some amount of NiWS phase. The high $\text{S}/(\text{Ni} + \text{W})$ value (table 3) in all catalysts (2.02–2.32), especially in the 5Ni20W one (3.00) should be marked. Sun *et al.* have reported the ratio $\text{S}/(\text{Ni} + \text{W})$ of 1.76 for the fully sulfided catalyst [30]. The observed S/W ratio is also higher than 2. Such high value of S/W in our catalysts could be explained by the presence of sulfur in different states in addition to the sulfur in the WS_2 -phase [4] and in nickel sulfide.

The $\text{S}2p_{3/2}$ binding energies are given in table 2. The binding energy of about 161.2 eV corresponds to S^{2-} ligands and/or terminally bonded disulfide S_2^{2-} [31].

The $\text{S}2p$ line decomposition ($\text{S}2p_{3/2}$ and $\text{S}2p_{1/2}$ components) has been made for the 5Ni20W catalyst, where the S/W and $\text{S}/(\text{Ni} + \text{W})$ ratios are the highest (figure 5).

The component on the lowest energy side ($\text{S}2p_{3/2} = 161.8$ eV) may correspond to S^2 ions as in NiS and WS_2 [31, 32]. Two doublets of the $\text{S}2p$ line with BE of

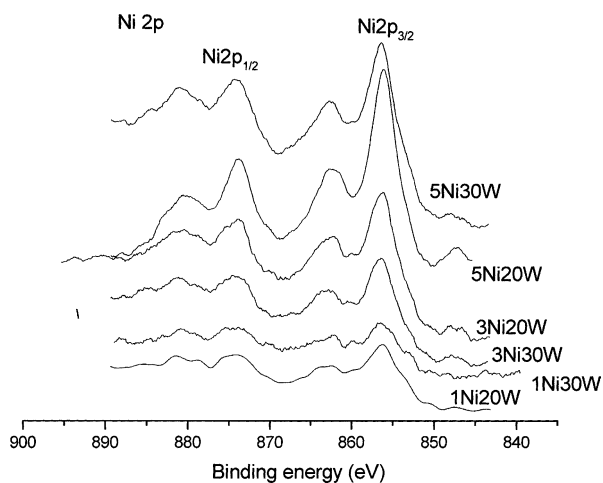


Figure 3. Ni2p photoelectron spectra for NiW / γ -Al₂O₃ catalysts calcined at 400 °C.

163.7 and 162.6 eV could be assigned to the S₂²⁻ pairs and to S²⁻ sulfur ions in WS₃ compound in accord with Martinez *et al.* [33]

The broadness of the signals at 162.6 and 163.7 eV could be also connected with the presence of a small amount of polysulfides with bridging S₂²⁻ ligands [31, 32]. Presence of elemental sulfur gives features at 165.3 eV (S2p)[32].

Due to the high values of S/(Ni + W) (table 3) that were observed in 5Ni20W catalyst (for comparison, S/W for the standard WS₂ is 2.26) we suggest that sulfidation of W to WS₂ proceeds through intermediates: a WS₃ phase and/or an oxysulfide species. The XPS results mentioned above (figure 2) confirms it.

Payen *et al.* also reported that WS₃ phase is probably a mixed with an oxysulfide species [18].

The observed sulfur states likely exist in all catalysts. Some of them are not observed in XPS spectra, because of their low concentration.

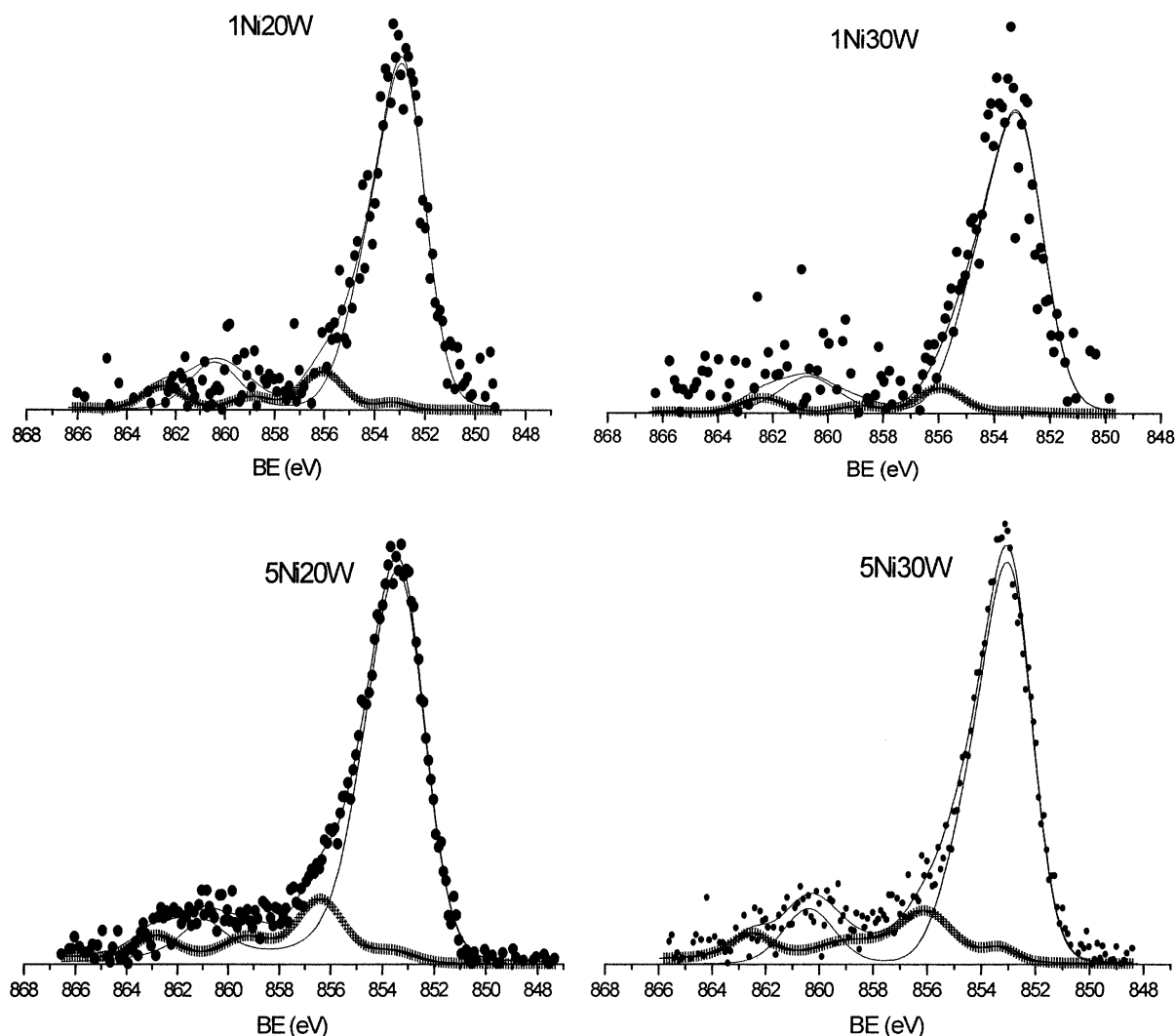


Figure 4. XPS fit result of Ni2p after sulfidation.

Table 3
Surface atomic ratios for the oxidic and sulfided catalysts and standards

Sample	Ni/Al		W/Al		W/Ni		Ni + Ni + W		S/Ni + W
	ox	sulf	ox	sulf	ox	sulf	ox	sulf	
2.4Ni	0.006	0.003							
20W			0.07	0.07					
1Ni20W	0.01	0.01	0.07	0.08	7.69	8.59	0.19	0.12	2.32
3Ni20W	0.02	0.02	0.06	0.10	2.88	4.62	0.33	0.22	2.24
5Ni20W	0.02	0.01	0.06	0.06	2.75	4.26	0.45	0.36	3.0
1Ni30W	0.02	0.02	0.09	0.10	5.58	7.10	0.093	0.085	2.20
3Ni30W	0.02	0.02	0.06	0.14	3.88	8.30	0.28	0.17	2.11
5Ni30W	0.04	0.04	0.10	0.13	2.77	3.48	0.34	0.28	2.02
Standard									
NiO							1	1	1.63
NiWO ₄							0.52	0.41	2.70
Ni _{0.17} W _{1.04} O ₄							0.14	0.10	2.83
WS ₂									2.26

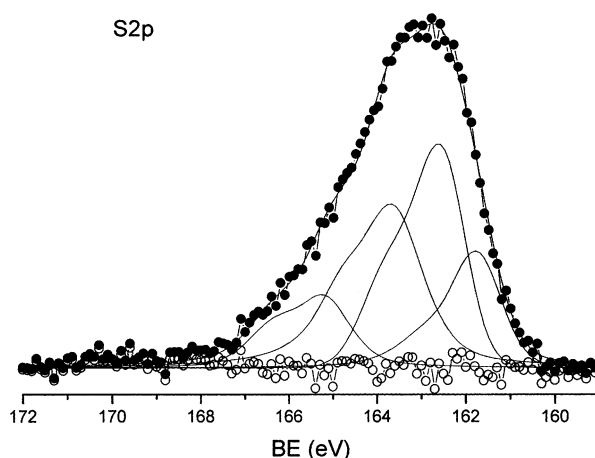


Figure 5. Decomposition of S2p XPS spectra of 5Ni20W catalyst.

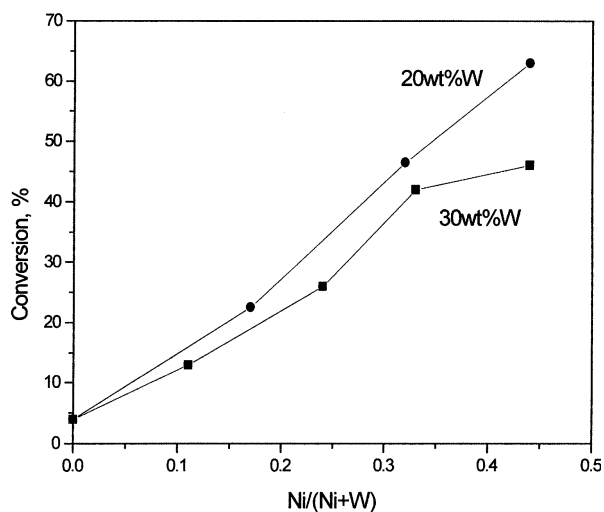


Figure 6. Thiophene conversion in IDS reaction as a function of Ni/(Ni + W) ratio.

3.3. Catalytic activity

The W/Al₂O₃ and Ni/Al₂O₃ catalysts revealed a very low activity (thiophene conversion about 5%) but Ni introduced simultaneously with W showed strong promoting effect (figure 6).

The activity of the catalysts with 20 wt%W increased about 15 times at the Ni/(Ni + W) ratio = 0.44. Almost proportional increase in activity of the samples with lower W concentration (20 wt%) we ascribe to growing amount of nickel polytungstates when the Ni content increases in the catalyst. It is known that the reduced phase is more easily sulfided. TPR data have shown lower reduction temperature of suggested polytungstate phase than that of its mixture with NiWO₄ phase (figure 1), i.e. polytungstate phase transforms into active NiWS phase more easily than the other ones.

In catalysts with higher W concentration HDS activity increases proportionally up to Ni/(Ni + W) = 0.33. Somewhat lower activity of these catalysts in comparison

with those having 20 wt% W could be related to lower dispersion of the formed NiWS phase and/or to more difficult sulfidation of NiWO₄ phase. Activity of the 5Ni30 catalyst is higher than would be expected. It could be related to presence of the NiS separated phase, which can be active phase itself and assist as well in the formation of some amount of NiWS phase. We can suggest that separated NiS phase leads to higher hydrogenation activity of 5Ni30W catalyst (table 1). No essential Ni influence on selectivity of the catalysts (in butenes hydrogenation) occurs in the catalysts with 20 wt% of tungsten.

4. Conclusion

In the calcined NiW/ γ -Al₂O₃ catalysts (20 and 30 wt% W, 1–5 wt% Ni) several phases coexist: nickelpolytungstates, NiWO₄, NiAl₂O₄-like spinel and NiO particles, concentrations of which depend on the Ni/(Ni+W) atomic ratio in the catalysts. Their inhomogeneity is confirmed by TPR data.

The XPS data of calcined samples indicated the presence of Ni well dispersed in tungsten oxide matrix with feature which can be ascribed to Ni in a separated nickel oxide particles and nickel containing species in contact with alumina support. The sulfidation of the catalysts leads to a systematic decrease in the Ni/(Ni+W) ratio as a result of transfer of W species to surface. Ni2p line position suggests formation of the active phase obtained after sulfidation of NiWO₄ and nickelpolytungstate compounds.

The Ni synergistic effect in the HDS reaction is confirmed by the increase of the HDS activity (~10–15 times). This effect is ascribed to formation of NiWS phase of high dispersion from mixed NiW oxide phases and the redistribution of active components in NiWS phase at higher Ni/Ni+W ratio.

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