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Tungsten/Alumina Catalysts: Effect of $H_3PW_{12}O_{40}$ Countercation on Surface Properties and Hydrodesulfurization Activity[1]

A. A. Spojakina*, K. Jiratova, N. G. Kostova*, J. Kocianova**, and M. Stamenova***
** Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
*** lnstitute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic*
e-mail: kiyky@ic.bas.bg
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Abstract—$H_3PW_{12}O_{40}$ heteropoly acid (HPW_{12}) and its Co, Fe, Ni salts supported on alumina have been used to model hydrodesulfurization catalysts of different activity. All catalysts revealed a promoting effect of the countercation in thiophene hydrodesulfurization, that of the nickel cation being the highest. The catalysts were characterized by measurements of surface area, HDS activity, TPR, FTIR, and DR spectra. IR spectra confirmed an effect of the countercation on the phase composition of the supported heteropoly compounds. 12-Tungstoaluminate heteropoly anions and coordinately unsaturated anions of HPW_{12} were detected in the IR spectra of the catalysts. The hydrotreating activity of the catalysts was proportional to the amount of hydrogen consumed in the range 20–500°C during TPR.

INTRODUCTION

The improvement of our life-environment is closely connected with better control of sulfur and nitrogen compounds and aromatic hydrocarbon emissions from petroleum derivatives into the air. Better hydrorefining catalysts having higher activity and selectivity can be key in solving the problem. Nowadays, it seems to be especially interesting to study W-containing catalysts because of their high activity in hydrogenation processes and stability at higher reaction temperature [1–6].

Tungsten catalysts are not so frequently studied as molybdenum catalysts. Compared to Mo-compounds, W-compounds show higher thermostability, which is especially important for their use in hydrotreating heavier fractions of petroleum. The hydrotreating activity of the catalysts depends on many factors that have not been fully investigated. It has been shown that the formation of surface compounds during synthesis of alumina-supported tungsten catalysts depends on tungsten loading, the presence of humidity, and pH at ZPC (zero point charge) of the support [7, 8]. Up to now, there is no clear opinion on the participation of the support in the formation and stabilization of active sites in alumina-supported Co (Ni)–Mo (W) oxide catalysts [9, 10]. It is also not evident whether the promoter forms active sites together with metals of Group VI (Mo, W) or whether it forms a separated active site [10, 11]. A study of heteropoly compounds as catalysts in hydrotreating processes could help to solve the problem [12, 13].

Heteropoly compounds can serve as a source of active components of hydrotreating catalysts. They can contain both fundamental and promoting elements (heteropoly anion and countercation) in a single compound of defined structure. Their use in a study of HDS catalysts is valuable and can give useful information for further improvement of the catalysts. Being precursors of an active phase in the investigated catalysts, heteropoly compounds could change their structure and composition because of their interaction with the support and/or during temperature treatment. Acid/base properties of the support and the type of heteropoly compound affect the occurrence and structure of the heteropoly compound in the designed catalyst. The countercation in the supported heteropoly compound can affect catalytic activity and the extent of the effect depends on the nature of the heteropoly compound, the properties of the support, and catalytic reaction as well. Some catalysts prepared from heteropoly compounds were also proposed as a novel efficient hydrodesulfurization catalyst. For example, a silica-supported monometallic tungstophosphoric acid, $H_3PW_{12}O_{40}$, is to be efficient in hydrodesulfurization of dibenzothiophene [14].

In this paper the $H_3PW_{12}O_{40}$ heteropoly acid (HPW_{12}) and its Fe, Co, Ni salts supported on alumina were used to model hydrodesulfurization catalysts of different activity.

EXPERIMENTAL

Catalysts (denoted as HW, FeW, CoW, and NiW) were prepared by impregnation of γ-Al_2O_3 (0.2–0.4 mm in size) with aqueous solutions of (HPW_{12}) acid or of corresponding synthesized salts. The latter were prepared by full substitution of hydrogen in HPW_{12} for the corresponding metal. All the catalysts contain about 1 mmol of heteropoly compound. A catalyst containing

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

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only Ni was prepared by impregnation of alumina with $NiNO_3$ water solution. All the samples were dried at 120°C for 4 h and calcined at 400°C for 2 h.

The surface area of the catalysts was measured (using the dynamic one-point BET method) from desorption of nitrogen that was adsorbed at –195°C.

IR spectra (400–1200 cm^{-1}) were recorded at room temperature on a Bruker IFS-25 Fourier transform IR spectrometer. The samples were pressed with KBr in a ratio of 1 : 150. Alumina absorption in the 400–1000 cm^{-1} range was compensated by subtraction of a normalized spectrum of the equivalent amount of support from the spectra of the catalysts.

Diffuse reflectance spectra (DRS) of the samples were recorded at room temperature on a Beckman 5270 spectrophotometer, equipped with a DR spectra accessory, in the wavelength range 240–800 nm. $BaSO_4$ has been used as reference. The spectra were evaluated by means of a Kubelka-Munk function $F(R)$.

TPR measurements were carried out in an apparatus described earlier [12]. The hydrogen/nitrogen mixture (10 mol % of H_2) was used to reduce samples at a flow rate of 17 ml min^{-1}. The temperature was linearly raised at a rate of 20°C min^{-1} up to 850°C.

Hydrodesulfurization of thiophene was measured in a continuous flow reactor at 350°C and atmospheric pressure. Each experiment was made with a fresh catalyst (0.2 g) that was standardized by *in situ* calcination in argon at 350°C for 0.5 h. Calcined catalyst was activated by sulfidation with H_2S (temperature 350°C, flow rate of 40 ml min^{-1}, 0.5 h). After activation had been completed, the catalyst was flushed with argon at the same temperature for 0.5 h, and then, feeding of the reaction mixture (6 mol % of thiophene in hydrogen, 25 ml min^{-1}) was started and the activity of the catalyst was measured for 4–5 h. The hydrogenation activity of the catalysts was characterized by butane/ΣC_4 ratios. More details are found in [12].

RESULTS AND DISCUSSION

The table presents the composition of the oxide forms of the studied samples and gives some texture data and activity in the thiophene conversion after 5 h. Surface areas of the catalysts prepared by impregnation of the support with heteropoly compounds decrease but do not differ from each other very much. Blocking of the narrow pore mouths of the support by a large anion of heteropoly acid [15] probably causes such a decrease in the catalyst surface areas. On the other hand, the Ni catalyst prepared by impregnation of the support with water solution of nickel nitrate shows an increase in surface area (235 m^2 g^{-1}).

The HW catalyst (HPW_{12} supported on alumina) shows low activity in thiophene conversion. HDS activity of the catalysts increases when metal cation is introduced into the molecule of heteropoly acid (Fig. 1). However, not all metals show the same promoting effect on catalytic activity.

Iron as a countercation reveals some promoting effect on catalytic activity in thiophene conversion at the start of the reaction, but shortly after reaching the maximum, the thiophene conversion decreases with a further increase in the time-on-stream value.

Cobalt as a countercation shows a higher effect on thiophene conversion than iron. Compared to the iron modified catalyst, thiophene conversion is relatively high from the very beginning of the reaction. With increasing time-on-stream value, the activity slightly decreases.

The highest increase in hydrodesulfurization activity is observed when nickel is used as a countercation of HPW_{12} acid (the NiW catalyst). The high activity

Surface area S_{BET} of the support and HDS catalysts, temperature maxima and amount of hydrogen consumed during TPR, HDS rate constant of pseudofirst order to thiophene k, and $g_{thiophene}$ h^{-1} g_{cat} and hydrogenation activity

Catalyst	M*, mg/g_{cat}	W, mg/g_{cat}	S_{BET}, m^2/g	TPR			w, g thiophene h^{-1} g^{-1} Cat	butane/ΣC_4
				T_{max}, °C	H_2^{**}, mM/g			
					20–800°C	20–500°C		
AD-I	–	–	185	–	–	–	–	–
HPW_{12}	–		–	471; 807	1.20	–	–	–
HW	–	189	151	524; >850	0.39	0.01	0.020	0.05
FeW	4.9	165	146	350; 530; >850	0.41	0.08	0.058	0.07
CoW	7.8	172	157	337; 560; >850	0.80	0.29	0.168	0.09
NiW	6.7	170	135	448; 788	3.33	0.55	0.314	0.28
Ni	9.9	–	235	346; 477; 667; >800	0.72	0.20	0.001	0.02

Note: *Amount of hydrogen (mmol/g) consumed.
**C_4 Hydrogenation activity.

does not change during the examined reaction time in spite of low nickel concentration in the catalyst. Initial thiophene conversion with this sample is about four times higher than that with the FeW catalyst and about twice as high as that with CoW. As the catalyst with a similar concentration of nickel but without tungsten shows practically no activity in thiophene conversion, catalytic sites active in this reaction have to be associated with tungsten and/or with species arising from the cooperation of tungsten and other metal cation.

The decrease in activity of some catalysts can be caused by the different stability of the individual phases appearing as precursors of active sites. The higher catalytic activity of the NiW catalyst could be explained by higher numbers of active sites formed with participation of nickel species.

Hydrogenation activity HYD expressed as the amount of butane found in the reaction mixture undoubtedly depends on the thiophene conversion, because hydrogenation of butenes proceeds after the splitting of thiophene and butane is the product of the subsequent hydrogenation reaction. The concentration of butane moved within the range 5–28 mol %, that observed with NiW catalyst being the highest (table). The catalysts FeW and CoW indicate similar hydrogenation ability. The great difference in butane concentration can be considered as proof of the highest hydrogenation ability of the NiW catalyst.

We attempted to examine whether some relation between catalytic activity and reducibility of the catalysts exists. The easiness of hydrotreating the catalysts to be reduced and sulfided is very important for their catalytic activity in a hydrotreating reaction. Catalytic activity was expressed as rate constant k (assuming a pseudofirst order of reaction with respect to thiophene) and analyzed its relation to the amount of hydrogen consumed during TPR measurements in the temperature range 20–500°C (table). All the catalysts prepared by impregnation of alumina with heteropoly compounds, whether they contained countercations or not, showed a linear relationship (correlation coefficient is 0.993).

The hydrogen consumption found in our TPR measurements (table) is connected with the reduction of both the tungsten phase and the cation system. The TPR pattern of the initial HPW_{12} acid showed two peaks with maxima 471 and 807°C, the first one being tiny. The high-temperature peak starts at 620°C. The total amount of hydrogen consumed in the temperature range 20–800°C was 1.20 mmol/g. The amount of hydrogen is a part of the total amount of hydrogen needed for complete reduction of HPW_{12} acid. The remaining reducible part of the acid obviously demands a reduction temperature higher than 800°C.

The HPW_{12} acid supported on alumina (the HW catalyst) showed a similar picture of reduction, and the maxima of both peaks are shifted to higher temperatures (the difference is about 50°C). It seems that supporting the acid over alumina causes stronger bonds between catalyst components and therefore more severe conditions of reduction.

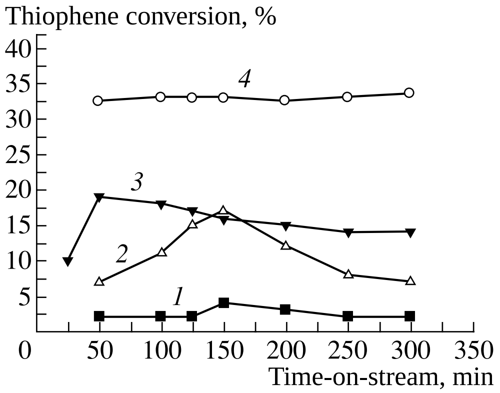

Fig. 1. HDS activity of tungsten-containing catalysts. (*1*) HW, (*2*) FeW, (*3*) CoW, and (*4*) NiW.

The total amount of hydrogen (in the range 20–800°C) for the FeW catalysts was approximately the same as that found for HW (table). The TPR patterns slightly differ in the temperature maxima of the peaks and in intensity of separated peaks. The TPR pattern of FeW in the high-temperature region resembles that of CoW. The low-temperature peak of FeW is slightly shifted to a higher temperature than that of the CoW catalyst. Probably it appears as result of the Fe^{3+} to Fe^{2+} reduction.

A sharp low-temperature peak appearing at about 346°C in the pattern of the Ni catalyst (Ni/Al_2O_5) originates from the reduction of surface nickel species. A separated NiO phase is probably not formed because of the low nickel concentration in our catalysts. It was confirmed by electronic spectra that octahedrally coordinated nickel species Ni_{oh}, i.e., nickel cations, are associated with the support surface [16]. At least three forms of reducible nickel particles were detected in the Ni catalyst (9.9 mg of Ni/g). The high-temperature peak in the TPR pattern of the Ni catalyst could be ascribed to reduction of so-called surface nickel aluminate, though its amount in the catalyst cannot be very high [17]. Overlapping of some peaks in the TPR patterns of Ni catalysts indicates the heterogeneity of the nickel species.

The reduction pattern of the NiW catalyst revealed both intense low- and high-temperature peaks appearing at 448 and 790°C. Compared to the Ni catalyst, the nickel phase in the NiW catalyst seems to reduce with difficulties (at higher temperatures). The total amount of hydrogen consumed by the catalyst is significantly higher than the sum of hydrogen amounts consumed during reduction of the corresponding Ni and HW catalysts. High-temperature reduction can probably include not only reduction of the tungsten component, but also the hardly reducible nickel compounds.

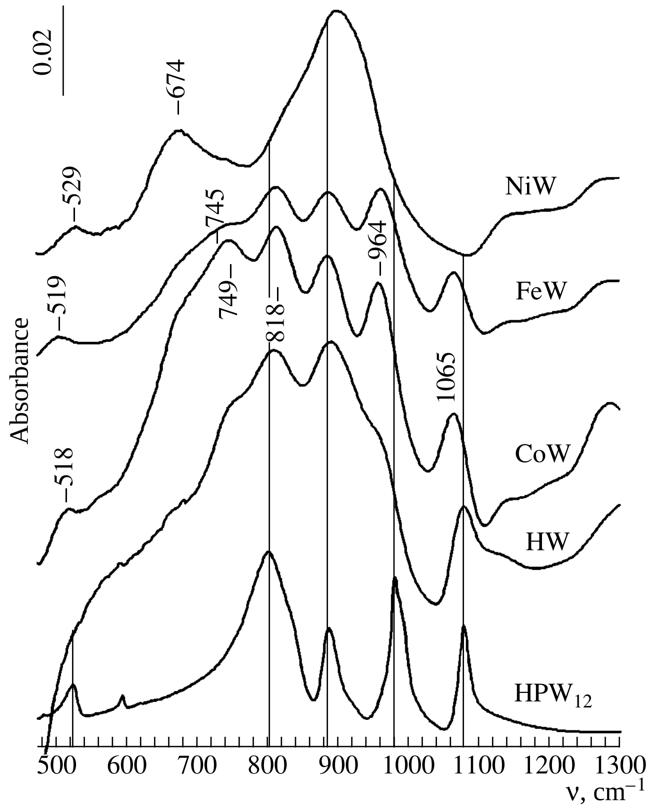

Fig. 2. FTIR spectra of initial HPW_{12} acid and alumina supported catalysts.

Interaction between the support and a metal compound during the preparation of Mo- and W-containing catalysts, as well as the formation of different new phases, was confirmed [18, 19]. The IR spectra of the initial HPW_{12} heteropoly acid and of our investigated catalysts are shown in Fig. 2. The spectrum of the initial acid shows bands at 1082 ($P–O_a$), 986 ($W=O_t$), 893 ($W–O_b$-W), 805 ($W–O_c–W$) $cm^{–1}$, the low intensive bands at about 598 and 525 $cm^{–1}$ characterizing the Keggin structure of the acid [20]. Spectra of the synthesized salts of HPW_{12} (not shown in Fig. 2) do not differ from that of the acid. However, when the synthesized heteropoly compounds are supported on alumina, their spectra change very substantially.

Compared to the spectrum of the initial heteropoly acid, the IR spectrum of the acid supported on alumina (Fig. 2, HW) shows overlapping of some bands and/or a decrease in their intensities. The P–O band in PO_4-group appearing at 1082 cm^{-1} somewhat enlarges. The W–O–W bands are overlapped revealing two maxima at 814 and 893 $cm^{–1}$ and shoulders at about 770 $cm^{–1}$. The intensity of the band at 960 $cm^{–1}$ of ν_{as} of terminal $W=O_t$ decreases and reveals itself as shoulder.

The effect of a countercation on the phases formed during their synthesis can be seen in the spectra of the prepared catalysts. The spectra of the CoW and FeW catalysts show bands at about 964, 888, 818, 750, and 519, partially overlapping, and a shoulder at about 640 $cm^{–1}$. The 1082 $cm^{–1}$ band is shifted up to 1075–1056 $cm^{–1}$, which can be ascribed to the formation of the coordinatively unsaturated (lacunar) heteropoly anion $[PW_{11}O_{39}]^{7–}$ and to its complex with the cation $PW_{11}M$ [21]. We can suppose a formation of analogues of the surface $PW_{11}Fe$ and $PW_{11}Co$ complex phase observed in [22]. The spectrum of NiW markedly differs from those of other catalysts. The absence of bands characterizing the PO_4-group of the $PW_{12}O_{40}$-anion in the NiW catalyst indicates destruction of a significant part of the $PW_{12}O_{40}$. New broad bands at 910, 674, and 529 $cm^{–1}$ occur. The absence of the characteristic bands of the $(WO_4)_{td}$ group (980 and 1022 $cm^{–1}$) [23] in the spectra indicates that the species with tungsten in tetrahedral coordination W_{td} are missing altogether in the catalyst. The band at 518 $cm^{–1}$ is attributed to δ(W–O–W) in complex $PW_{11}M$ [22], and its presence is noticeable in the spectra of the CoW and FeW catalysts and is weakly expressed for the NiW catalyst. The band position does not depend on the radius of M^{n+}. A weak band at 529 $cm^{–1}$ is revealed in the spectra of the NiW catalyst and probably reflects the formation of aluminum and nickel phosphates [24]. In addition, the new band at about 1130–1140 $cm^{–1}$, which is missing in the spectrum of the initial HPW_{12}, can be seen in all phosphorus-containing catalysts (Fig. 2, FeW, CoW, HW, NiW). Such a band could appear when formation of a surface $AlPO_4$-like species occurs [24, 25].

In all tungsten-containing samples, some bands appear in the 640–780 $cm^{–1}$ region. The appearance of the band depends on the presence of the metal ion in the heteropoly anion sphere only [22, 26]; i.e., the bands prove the formation of the W–O–Me bond. We noted the formation of such a complex in FeW and CoW samples. The findings indicate the disorder of the initial structure of the heteropoly compound and the formation of new phases arising due to interaction between the support and the loaded $PW_{12}O_{40}^{3-}$ anion. The formation of aluminum and tungsten-containing heteropoly compounds can be expected on the catalyst surface as a result of the reaction of W-species with dissolved Al-species (which arise from the alumina support during synthesis of the catalysts) [18, 27].

It has been reported [18, 28] that complexing of the aluminum and tungsten species leads to formation of aluminotungstic heteropoly anions of Keggin structure, in which the aluminum atom is placed in the central position of tetrahedra or substitutes one tungsten atom in the heteropoly anion. A mixture of products containing substantial amounts of $[AlW_{12}O_{40}]^{5–}$ and/or $[Al(AlOH_2)W_{11}O_{39}]^{6–}$ arises in the presence of aluminum and tungsten species [27, 28]. The aluminum ion shows a tetrahedral or octahedral state depending on its surrounding. The bands at 955 $cm^{–1}$ (W–O terminal bond), at 885 cm^{-1} with a small shoulder at 925 cm^{-1} (W–O–W edge sharing), at 810 cm^{-1} (W–O–W corner sharing), and at 770 cm^{-1} (Al–O stretching motion in the AlO_4 unit) were revealed in the IR spectrum of 12-tungstoaluminate acid ($H_5[AlW_{12}O_{40}]$) prepared by Nomiya and Miwa [29]. The shoulder at 770 cm^{-1} and the presence of other overlapping bands in the spectrum of our HW catalyst could confirm formation of an $AlW_{12}O_{40}^{5-}$ anion in accordance with Nomiya and Miwa [29]. The band at about 750 cm^{-1} can be seen especially clearly in the spectra of the CoW and FeW catalysts. Unfortunately, the mixed composition of the newly formed phases does not allow one to fully prove the presence of this anion. The aluminum ion can also be included in the lacunar heteropoly anion that arises, forming a $(PW_{11}AlO_{39})^{4-}$ complex with octahedral Al coordination. An increase in pH observed during hydrolysis of Al_2O_3 (table) helps to stabilize the formed lacunar heteropoly compounds in the investigated samples. The compounds that arise during catalyst preparation are consequently adsorbed on the support surface. After heat treatment, the supported W-containing compounds probably remain on the support surface as disordered analogues of polytungstate phases associated with the countercation and aluminum cation. As mentioned above, these phases could be mixed heteropoly anions with the cation inclusion instead of phosphorus and/or with substitution of W in the surrounding of the central P heteroatom [22, 27].

DRS of the calcined tungsten-containing catalysts are presented in Fig. 3. All the catalysts show an intense absorption band in the UV region at about 250–330 nm arising as a result of ligand–metal charge transfer $O^{2-} \longrightarrow W^{6-}$ [16]. The maximum intensity of the band is the same for the CoW and HW catalysts, but its position is shifted to a longer wave region with the NiW and FeW catalysts. Such shifting can be associated with the presence of Fe_{oh} and Ni_{oh}. The band at about 330 nm appears when nanosized Fe species are present [30]. So, the shifting of the W^{6+} charge transfer band could be explained by the presence of the Fe_{oh} band. A low-intensive diffuse absorption between 400–600 nm is also detected and is probably connected with partial reduction of Fe^{3+} ions. The shifted band of the NiW catalyst is overlapping with the band of d–d transfers of octahedral Ni^{2+} appearing at 400 nm [31]. Apart from the band starting at about 500 nm, a plateau at about 700 nm can be seen in the spectrum of the NiW sample. The plateau is not seen in the CoW catalyst spectrum, but a triplet of Co_{td} at 525–640 nm appears instead.

The Ni catalyst containing no tungsten shows bands with intensity maxima at 300, 405 (shoulder at 375 and 575 nm), and intense absorption at 650–750 nm with a maximum at 675 nm (Fig. 3b). All the bands are mainly related to octahedrally coordinated Ni^{2+} ions [16, 32]. The band at 300 nm ascribed to $NiAl_2O_4$ (other bands of $NiAl_2O_4$ occur at 600, 645, and 715 nm) could be overlapping with the bands of Ni_{oh}. In accord with Sheffer *et al.* [16], a small amount of nickel aluminate seems to appear in the Ni catalyst, though a high concentration of it in the catalysts cannot be highly expected. The reason is in the temperature of calcination: The compound is formed after heating at temperatures higher than 500°C [16] or 800°C [17], but our samples have been heated to 400°C.

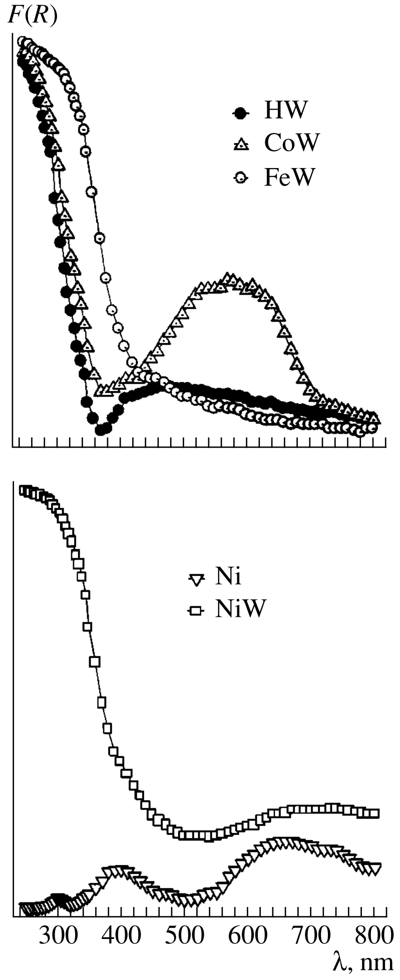

Fig. 3. DR spectra of alumina supported catalysts.

The DR spectroscopy results prove that the preparation method affects the phase composition of the hydrotreating catalysts. This is clearly seen when spectra of the NiW and Ni catalysts, especially their absorption backgrounds and diversities of the spectra in the 250–400 nm region, are compared. With the NiW sample (having low nickel concentration), the background of Ni bands is substantially higher, probably as a result of the extreme broadening of those Ni bands, which do not appear as prominent bands. The fact that nickel bands are not revealed in the spectra can be attributed to nickel inclusion in the molecule of the heteropoly compound, very likely, of newly formed mixed nickel containing species. IR spectra also prove the absence of the band characterizing the HPW_{12}-anion (Fig. 2).

The results of physical-chemical properties confirmed the considerably different surface properties of the NiW catalyst and higher dispersion of nickel incorporated as a countercation of heteropoly tungstic acid. The intimate cooperation of the nickel and the heteropolytungstic anion in the catalyst leads to a very active catalyst in thiophene hydrodesulfurization and to the highest activity in hydrogenation of reaction intermediates.

CONCLUSIONS

Tungsten/alumina catalysts prepared using various salts of 12-$H_3PW_{12}O_{40}$ acid show different activity in thiophene hydrodesulphurization depending on the countercation and the method of preparation.

A positive promoting effect of the countercation on the HDS activity was observed with all the metal ions examined (Fe, Co, Ni), but their effect manifested itself to different extents.

The nickel cation showed the highest promoting effect on the activity of the tungsten–alumina catalyst. The most important parameter influencing the activity of the NiW catalyst seems to be the presence of the highly dispersed nickel in the newly formed mixed polytungstate phase. The TPR results confirm this suggestion. This catalyst shows the highest HDS and hydrogenation activity.

The hydrotreating activity of the catalysts prepared from heteropoly compounds depended linearly on the amount of hydrogen consumed during TPR experiments between 20 and 500°C.

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