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Support effect on the properties of iron–molybdenum hydrodesulfurization catalysts

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Two series of Mo and Fe containing catalysts have been prepared over alumina and titania supports using $H_3PMo_{12}O_{40}$ heteropolyacid (HPMo) and Fe salt of HPMo. Catalysts have been characterized by BET, SEM, IR, TPR, XPS methods and by their HDS activity in the reaction of thiophene conversion. The TiO_2-supported catalysts with low Mo concentration (6 wt%) show higher HDS activity than the catalyst with 12 wt% Mo. Iron promoting effect (Fe/Mo ~ 0.1) is observed with both, the alumina- and titania-supported catalysts. Iron supported over alumina increases Mo reducibility and decreases it on TiO_2-supported catalysts. Compared to alumina-supported catalysts, the TiO_2-supported catalysts show higher surface concentration of Mo^{6+} and Mo^{5+} in octahedral coordination – Mo(Oh). Iron increases the Mo(Oh) concentration even more. After sulfidation the Fe-containing catalysts show formation of different Mo valence states (Mo^{4+}, Mo^{5+}, Mo^{6+}), Fe–P, Mo–P and/or Fe–Mo–P bonds, which affect the HDS catalytic activity.

KEY WORDS: heteropolycompounds; titania and alumina supports; iron promotor; thiophene conversion; IR; TPR; XPS; SEM.

1. Introduction

Stricter environmental regulations have driven the reduction of sulfur, nitrogen and aromatics to a minimal level in fuels, a trend that will be world-wide in the coming years, i.e. a target of about 15 ppm in diesel by 2010 and sulfur reduction in gasoline had to reach about 50 ppm by 2006. Thus, in order to comply with these norms, the oil industry has been improving the performance of the hydrotreating process [1]. Therefore, refiners are looking for new catalysts with better activity as one of the most important ways to decide this problem. Sulfided Co(Ni)–Mo(W) catalysts have traditionally been used for hydrotreating processes. Generally these catalysts have been supported on Al_2O_3. There have been various attempts to improve catalyst activity such as changes in active metal composition, additives and supports. Among them the variation of support composition is one of the most promising approaches [2,3].

In the last years some studies have suggested that the nature of the supports plays role in the determining the activity of the catalysts. The support must have appropriate textural and mechanical properties, high temperature stability and high surface area in order to ensure high dispersion of the active compounds. Many authors have studied effect of the supports on HDS activity. Those have used: Al_2O_3, SiO_2, zeolites, clays, TiO_2, Al_2O_3–SiO_2, Al_2O_3–TiO_2 mixed oxides and others [4,5]. In spite of variety models proposed to explain the nature of the catalytic sites in these catalysts none of these models can explain the role of support [3].

Numerous investigations of various supports for the HDS catalysts showed that titania as well as ZrO_2, supported catalysts possess higher initial activity than the alumina-supported catalysts. Though the finding seems to be very interesting [6,7], the reasons for the increased activity of the TiO_2 supported catalysts are still unclear.

Elucidation of the promotors role is important and promising possibility to tailor the properties of the catalysts. Commonly used promotors in molybdenum/tungsten HDS catalysts are cobalt or nickel. The synergetic effect of the Co(Ni) in the HDS catalysts and the effect of support on it need further elucidation [5].

In this aspect, the effect of other promotors is worth studying. An example of the potentially interesting promotor of the Mo catalysts is iron. Earlier it has been found hat the sulfided iron-containing phase, well dispersed on a carbon support, has promising properties as the hydrotreating catalyst [8–10]. The alumina-supported FeMo catalysts are less active in the HDS of thiophene than carbon-supported catalysts. The iron concentration has very strong impact on HDS activity of the iron–molybdenum–alumina catalysts [11].

Our studies of Mo-containing catalysts over SiO_2 and TiO_2 supports have shown that during the catalyst preparation process Mo heteropolycompounds are formed that are very likely precursors of the active sites for the thiophene HDS [12,13].

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Recently, the increased number of studies on the application of heteropolycompounds (HPC) (polyoxometalates) or their precursors as HDS catalysts has appeared. Griboval *et al.* [14] have synthesized new salts of heteropolyacids having Keggin-type structure and used them for preparation of the HDS catalysts. These compounds are very attractive models of oxide-supported catalysts since they can be regarded either as oxide clusters with controlled nuclearity and composition or as precursors of the supported oxide phase obtained after thermal decomposition of the HPC. In the last case the knowledge of the transformation mechanism of the HPC into oxide is paramount to control the nature of the active oxide phase obtained after decomposition of supported heteropolycompounds species.

The resulting oxide phase is formed from clusters with the same nuclearity and composition as those of the HPC precursor. This phase is result of the aggregation of oxides species originated from the HPC precursor [15]. From this point of view, we can expect that a well-dispersed precursor species will lead to a well-dispersed oxide phase after thermal decomposition of the HPC. The dispersion of the species adsorbed on the surface should roughly depend on two types of attractive interactions:

- Interaction between species themselves;
- Interaction between support surface and species.

If the former interaction is the most important, as in the case of water on a no wet surface, aggregates will be obtained, whereas if the latter is predominant, a monolayer-like deposit with high dispersion will be obtained.

The HDS activity and stability is also affected by the different additives, especially, phosphorus [12]. Its effect on the catalysts properties also needs in explaining. The positive role of phosphorus for improving of the properties of HDS catalysts is also known [16]. The promoting phosphorus influence on the HDS catalysts of different composition continues to take attention [17].

That is why the use of heteropolycompound containing all active components in one molecule, loaded on the chosen support to study the joint effect of the active metal, promotor and phosphorus on the properties of the HDS catalysts, seems to be very interesting.

In this paper, the effect of the support, method of preparation and activation of FeMo catalysts on the phase composition and catalytic activity and selectivity in thiophene HDS is studied.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by incipient wetness impregnation of Al_2O_3 (200 $m^2\ g^{-1}$) and TiO_2 (anatase, 75 $m^2\ g^{-1}$) with aqueous solution of $H_3PMo_{12}O_{40}$ heteropolyacid (HPMo) and its Fe salt. The catalysts are denoted as HPMo-12/Al, HPMo-6/Al, HPMo-12/Ti and HPMo-6/Ti, where Al, Ti mean Al_2O_3 and TiO_2. The numbers show the molybdenum content in wt%. The Fe salt of HPMo (FePMo) was synthesized by full substitution of hydrogen in HPMo using $Fe(NO_3)_3$ in a stoichiometric quantity. In the Fe-containing samples 0.5FePMo-12/Al, 0.25FePMo-6/Al, 0.5FePMo-12/Ti and 0.25FePMo-6/Ti the numbers before Fe mean the iron content in wt%. All catalysts were dried 4 h at 378 K and calcined 2 h at 623 K.

2.2. Catalysts characterization

2.2.1. BET surface area

The surface area of the catalysts was estimated by measuring of the adsorption–desorption isotherms of nitrogen at −78 K (BET method).

2.2.2. IR spectra

IR spectra (400–1200 cm^{-1}) were recorded at room temperature on a Bruker IFS-25 Fourier transform IR spectrometer. The catalysts were pressed with KBr in ratio 1:150. Alumina and titania absorption in the 400–1200 cm^{-1} range was compensated by subtraction of a normalized spectrum of the equivalent amount of support from the spectra of the catalysts [18].

2.2.3. SEM photographs

Scanning electron microscope (SEM) JSM-5300, Jeol, was used to study the morphology of the deposited cover in oxide form. The photographs were taken in the regime of secondary electrons SEI.

2.2.4. TPR measurements

TPR measurements were carried out in an apparatus described earlier [19]. Hydrogen/nitrogen mixture (10 mol% H_2) was used to reduce catalysts at the flow rate 17 $cm^3\ min^{-1}$. The temperature was linearly raised at a rate of 20 K min^{-1} from 293 K up to 1123 K.

2.2.5. XPS measurements

XPS measurements were performed with an ESCALAB-Mk II (VG Scientific) electron spectrometer. Samples were excited with MgK0 Kα radiation (hν = 1253.6 eV), operating at 12 kV and 20 mA. The residual pressure inside the analysis chamber was below 5×10^{-9} Torr. The binding energy (BE) of O1s, Al2p, Mo3d, Ti2p, Fe2p, P2p and S2p core electron levels were determined by computer fitting the measured spectra and were referenced to the C1s XPS signal at 284.6 eV. The binding energies are accurate within 0.1 eV. In order to obtain information on the structure of the surface and the dispersion of the active phases the surface atomic ratios were calculated as the ratio of the corresponding peak intensities, corrected with theoretical sensitivity factors based on Scofield's photoionization cross-sections [20]. The Mo 3d and S 2p lines were decomposed using an iterative least-squares computer program, the curves being taken as 85% Gaussian and 15% Lorentzian. The spin-orbit splitting of the Mo 3d and S 2p peaks was 3.15 and 1.74, respectively.

2.2.6. *Catalytic activity*

HDS of thiophene was carried out in a continuous flow reactor at 623 K and at 0.1 MPa. Each experiment was carried out with a fresh catalyst (0.1 g) that was standardized by *in situ* calcination (30 min) in argon at 623 K. Calcined catalyst was activated by sulfidation with a mixture of H_2S + H_2 during 1 h at temperature 623 K and flow rate 40 cm^3 min^{-1}. We have found out in our preliminary experiments that this sulfidation treatment gives maximal catalytic activity of the catalysts. After the activation of the catalyst had been completed, the catalyst was flushed (30 min) with argon at the same temperature, and then, the reaction mixture (6 mol% of thiophene in hydrogen) with WHSV of thiophene 2 h^{-1} was fed into the reactor. Activity of the catalyst has been measured for 5 h. It was expressed as the thiophene conversion to hydrocarbons (C_4). The hydrogenation selectivity of the catalysts was evaluated by the ratio of concentration of normal butane to the sum of C_4 compounds ($n-C_4/TC_4$) in the reaction products.

3. Results

3.1. *BET surface area*

Table 1 gives the survey of the catalysts prepared and some of their characteristics. It can be seen that the surface area of the TiO_2 support (75 m^2 g^{-1}) decreases negligibly after loading molybdenum compounds while the concentration increased up to 12 wt% Mo. The surface area of Al_2O_3 (200 m^2 g^{-1}) changes significantly after supporting the same range of Mo concentration in agreement with the results published earlier [21].

Table 1
Description of catalyst samples and TPR data

No.	Catalysts	S_{BET} (m^2 g^{-1})	Mmol[a] H_2 g^{-1}	Mmol[b] H_2 g^{-1}	T_{max} (°C)
Support (Al_2O_3) – S_{BET} – 200 m^2 g^{-1}					
1	HPMo-6/Al	150	0.789	0.989	490, 817
2	FePMo-6/Al	178	1.002	1.092	490, 825
3	HPMo-12/Al	157	0.860	1.452	477, 813
4	FePMo-12/Al	180	1.110	1.821	468, 795
Support (TiO_2) – S_{BET} – 75 m^2 g^{-1}					
1	HPMo-6/Ti	68	1.624	2.424	453, 749
2	FePMo-6/Ti	72	1.033	1.587	467, 671
3	HPMo-12/Ti	67	2.601	4.563	488, 760
4	FePMo-12/Ti	65	1.552	2.506	501, 773

[a] In the temperature range 293–923 K.
[b] In the temperature range 293–1093 K.

3.2. *SEM*

SEM results indicate that molybdenum species are dispersed as a monolayer in the oxidic form of the Mo/TiO_2 catalyst. The HPMo-6/Ti catalyst has molybdenum particles randomly distributed over the support surface without defined size of the particles. When concentration of molybdenum increases up to 12 wt%, the support surface is covered with a dense multi-layer. SEM results (figure 1) show non-homogeneous distribution of the active phase precursor over the surface of both supports with 12 wt% Mo.

Apart from the observed high Mo dispersion, Mo species probably depress the aggregation of the anatase particles. XRD detects no transformation of anatase to rutile. The same effect was noticed in the paper [22].

In the alumina-supported catalysts aggregates formed from the particles of different sizes, combined in multilayers, when the Mo concentration increases up to 12 wt%. In the low-concentrated catalyst HPMo-6/Al these aggregates are dispersed homogeneously.

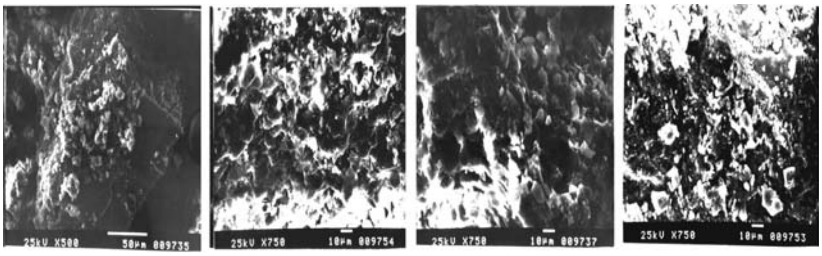
3.3. *Catalytic activity*

The results of catalytic activity tests are presented on figure 2.

The activity presented in figure 2, shows its dependence on the support used, the active component concentration (molybdenum) and the promotor presence (iron). From the first view the activity of the TiO_2 supported samples is higher in comparison to the alumina supported. This is detected especially clearly at the low Mo concentration (6 wt%) – 11% and 27% thiophene conversion for HPMo-6/Al and HPMo-6/Ti, respectively. The activity of the sample HPMo-12/Ti is higher than that of the HPMo-12/Al only quite little.

The Fe introduction as the counteraction increases activity of all samples while the value of this effect depends on the support used and the components concentration. In case of 0.25 wt% Fe increases activity of the low concentrated TiO_2 supported catalyst only with 8%, whereas on the low concentrated Al_2O_3 supported catalyst activity grew two times.

Having in mind the dependence of the HDS activity of the TiO_2-supported catalysts on Mo concentration [23,24], the catalysts containing 6 and 12 wt% Mo have been studied. The HPMo-6/Ti catalyst shows about three times higher activity (related to 1 mol Mo content) in comparison to that of the catalyst with 12 wt% Mo. The HDS activity of the alumina-supported catalyst HPMo-6/Al is more two times lower than that of the titania supported low-concentrated catalyst. At high molybdenum concentration (12 wt% Mo), both, the HPMo-12/Ti and HPMo-12/Al catalysts, showed nearly equal thiophene conversion. Different catalytic behavior



HPMo-12/TiO_2 HPMo-6/TiO_2 HPMo-12/Al_2O_3 HPMo-6/Al_2O_3

Figure 1. SEM photography of catalysts.

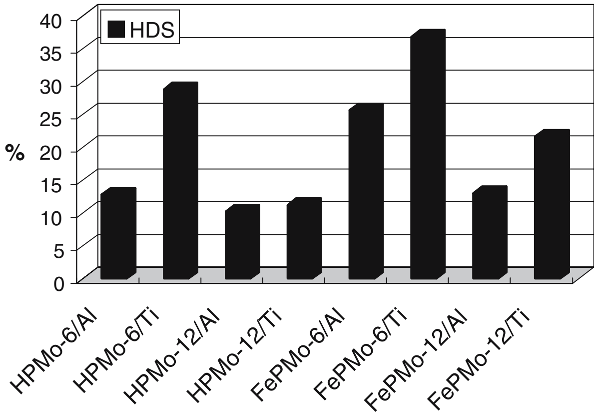


Figure 2. HDS conversion of the TiO_2 and Al_2O_3 supported catalysts (%).

of the low- and high-concentrated Mo catalysts confirms the support effect at low Mo concentration only.

The titania-supported catalyst containing iron in the form of the counteraction of HPMo acid (0.5FePMo-12/Ti) shows approximately higher thiophene conversion in comparison to that of the HPMo-12/Ti catalyst. The corresponding alumina-supported catalyst (0.5Fe-PMo-12/Al) demonstrated the increase in HDS activity about 1.5 times.

The effect of iron is not so pronounced when concentration of Mo is low (6 wt%). In this case, the iron effect is likely overlapped with the support effect.

3.4. TPR data

The TPR data are given on figure 3.

TPR profiles of the catalysts supported on both the alumina and TiO_2 reveal two peaks with slightly different $T_{\max}$. The values of $T_{\max}$ of the catalysts depend on the support and Mo concentration: The first $T_{\max}$ on the titania about 726 K shifts to higher temperature in the presence of the counteraction (the sample FePMo-6/Ti) and at increasing of the component concentration.

The high temperature peak in the TiO_2 supported samples appears at about 1023 K and is shifted to higher temperatures in the Fe presence and higher concentration of the components. The H_2 consumption is lower in comparison with that of the catalyst without iron (table 1).

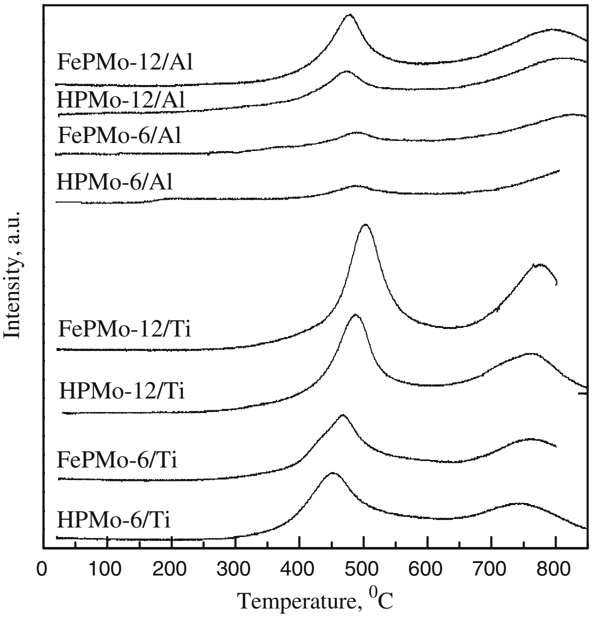


Figure 3. TPR profiles of catalysts.

In the alumina supported catalysts the first peak is shifted to lower temperature whereas the second one to higher. This peak is unfinished in the studied region of temperatures. A contrary to the titania supported catalysts the H_2 consumption is lower, although it increases slightly in the Fe-containing samples.

3.5. IR spectra measurements

IR spectra of the initial HPMo acid and that of the prepared catalysts are presented on figure 4.

In the spectrum of the initial HPMo acid, the characteristic bands of the Keggin-type heteropolyacids at $\sim$964 cm^{-1} (Mo = O), 785, 870 cm^{-1} (Mo–O–Mo), 1064 cm^{-1} (P–O) are observed [18].

Disappearance of the bridge Mo–O–Mo bonds (785 cm^{-1}) and a shift of the band appearing at $\sim$965 cm^{-1} (Mo = O) in the spectra (figure 4) of both HPMo-12/Al and 0.5FePMo-12/Al demonstrates interaction of HPMo acid with alumina. The new bands at $\sim$660 and 445 cm^{-1}, characteristic of the Mo–O–Mo groups in the spectra of the Anderson type heteropolymolybdate (analogue of the $[AlMo_6O_{24}H_6]^{3-}$ anion),

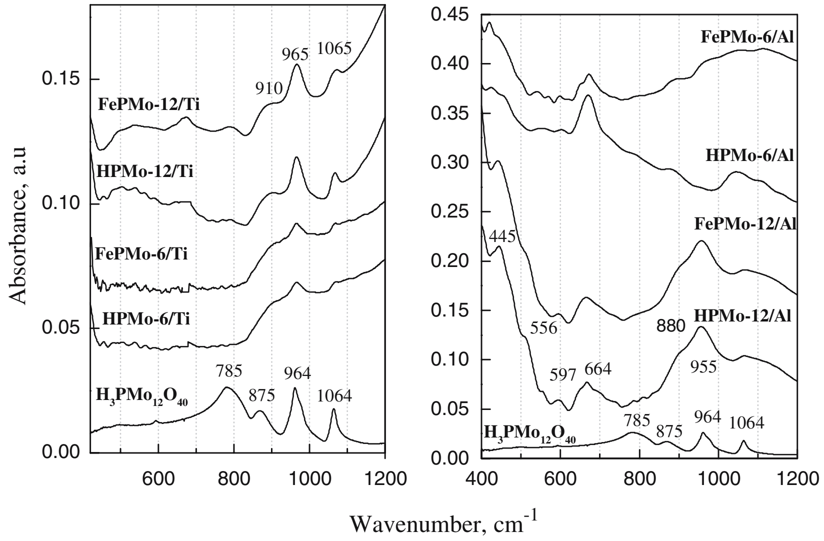


Figure 4. IR spectra of samples.

and a band in the region 880–950 cm^{-1} (terminal Mo = O group [18,25]) are visible in the spectra of the catalysts. Appearance of the intense band at ~445 cm^{-1} also points out the presence of aluminum molybdate and aluminum heteropolymolybdate [26] in the catalysts. The shoulders at 880 and 990 cm^{-1} in the region 850–1000 cm^{-1} and the low intense band (590 cm^{-1}) demonstrate formation of MoO_3 on the alumina support [27].

The obtained IR spectra confirm formation of aluminum heteropolymolybdate during synthesis of the catalysts, which is stable after calcining at 623 K. Enlargement of the band at ~1065 cm^{-1} and appearance of the band at ~1100–1200 cm^{-1} confirm formation of aluminum phosphate [26].

Disordered defect Keggin structure was detected on the surfaces of the TiO_2-supported catalysts from the doublet bands appearing at ~965 and 1065 cm^{-1} (characteristic of the heteropolyacids). However, several significant changes in the spectrum of the initial acid can be seen. Instead of the band at ~870 cm^{-1} a new broad band at 850–920 cm^{-1} appears. It probably comes from the overlapping of the bands characteristic of different phases that could not be separated. In accordance with the data [28] we can suppose that the $[PMo_{12}O_{40}]^{4-}$ anion, analogue of $[TiMo_{12}O_{40}]^{4-}$ anion, and the Mo = O bonds coming from the tetrahedral $MoO_4{}^{2-}$ groups (the bands at 890 and 908 cm^{-1}) give bands in this region of the spectra. The band at 916 cm^{-1} which Iwasawa *et al.* [29] assigned to Mo = O bond coming from Mo^{6+} in tetrahedral (Td) or octahedral (Oh) position, could also exist in the catalyst spectrum. MoO_3 phase was not identified in the spectra of the TiO_2-supported catalysts [24] and instead, a new band at 674 cm^{-1} appeared. Presence of the new band in the 400–700 cm^{-1} region is observed [25] when Mo (W) is substituted for transition metal ion in the heteroatom surroundings. Therefore, we can suppose formation of Fe substituted heteropolyanion as well as substitution of Mo for Ti in the loaded HPMo heteropolyanion.

3.6. X-ray photoelectron spectra

3.6.1. Oxides forms

XPS of the calcined HPMo-12/Al (figure 5a) and the HPMo-12/Ti catalysts (figure 5c) show two Mo3d doublets with $Mo3d_{5/2}$ binding energy (b.e) of 232.6–233.7 eV assigned to presence of Mo^{6+} ions in different oxygen surrounding [30–33], in octahedral (Oh) (232.5 eV) and tetrahedral (Td) oxygen coordination (233.6) [32,33]. Suitable Mo compounds have been observed in the IR spectra (figure 4). Effect of the support on the Mo state is revealed by the peak with b.e of 231.4 eV in the spectrum of the HPMo-12/Ti sample which is assigned to Mo^{5+} ions [34] as well as a higher concentration of the Mo^{6+}(Oh) and a lower of the Mo^{6+} (Td). The value of Mo^{6+} ions binding energy is higher than that mentioned in literature [35]. It can been explained by existence of the surface Mo species in heteropolycompounds that show higher Mo binding energy value than other Mo compounds [36].

The Mo3d spectrum (figure 6a) of the 0.5FePMo-12/Al catalyst shows no essential change the molybdenum state (b.e. of two dublets is 232.7 and 233.8 eV), whereas curve-fitted Mo3d spectra of the iron-containing titania supported catalysts show narrow peaks of Mo (Oh) and Mo (Td) with b.e. of 233.0 and 233.9 eV, respectively (figure 6c) but the Mo^{5+} peak is absent in the spectrum.

The b.e. of the Fe2p (710.1–711.0 eV) corresponds to Fe^{3+} ions [37] in the catalysts on the both of the supports. However, the molar Fe/Mo ratio observed in the TiO_2-supported catalysts (oxides form) is higher significantly than that in the corresponding alumina-supported ones.

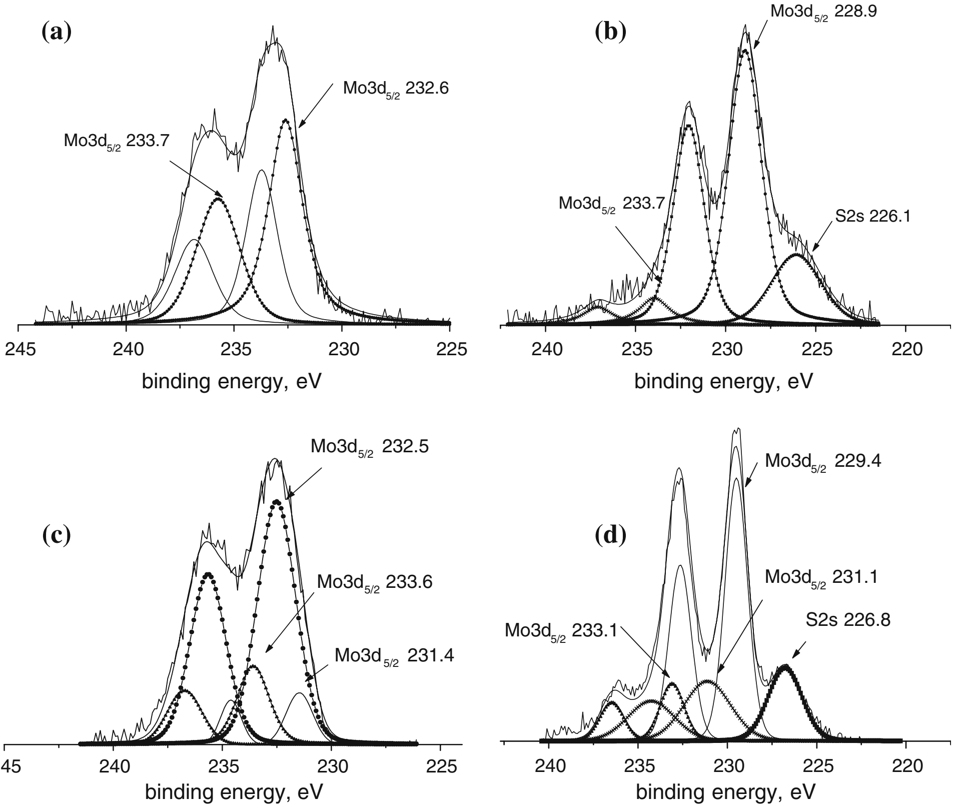


Figure 5. The curves fitted Mo3d spectra in oxidic and sulfided forms of the HPM supported on Al_20_3 (a, b) and TiO_2 (c, d).

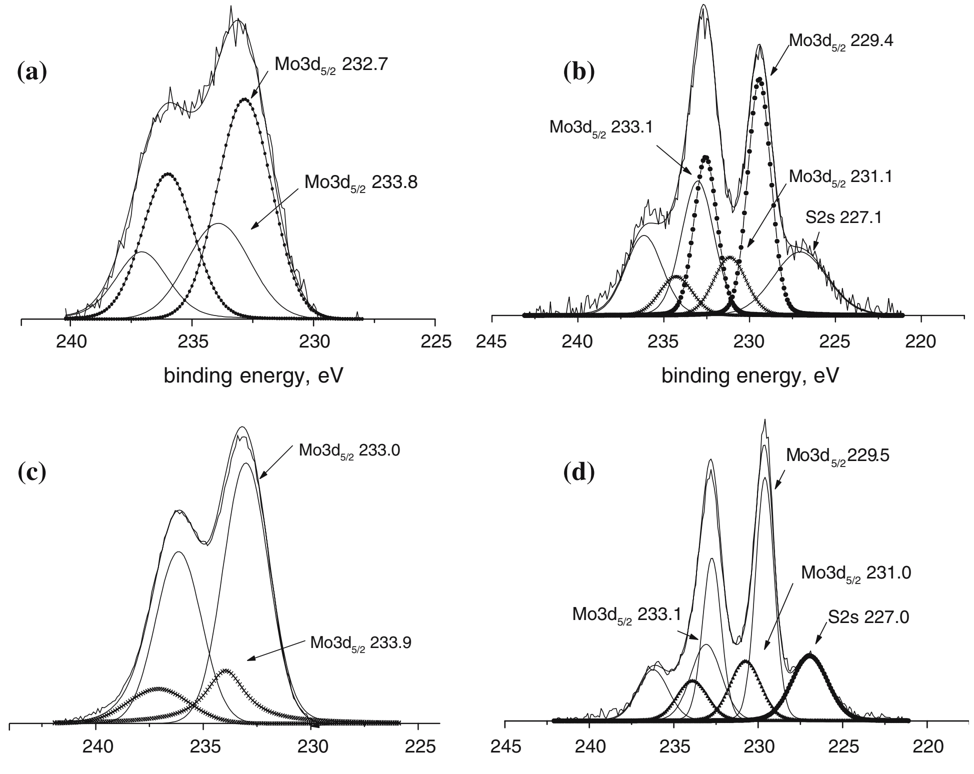


Figure 6. The curves fitted Mo3d spectra in oxidic and sulfided forms of the FePM catalysts supported on Al_20_3 (a, b) and TiO_2 (c, d).

Table 2
XPS data of the catalysts

Sample*	Form	Surface atomic concentration (%)						
		Mo3d	Fe2p	Ti2p	Al2p	O1s	P2p	S2p
HPMo-12/Al	Oxide	1.91	–	–	34.5	63.2	0.36	–
	Sulfide	1.32	–	–	47.5	48.8	–	2.21
FePMo-12/Al	Oxide	2.56	0.31	–	39.70	57.41	–	–
	Sulfide	2.23	0.03	–	40.37	53.21	–	3.34
HPMo-6/Al	Oxide	1.24	–	–	42.6	56.0	–	–
	Sulfide	1.05	–	–	41.5	55.9	–	2.10
FePMo-6/Al	Oxide	1.33	0.15	–	36.8	61.8	–	–
	Sulfide	1.65	0.22	–	37.2	59.8	–	3.05
HPMo-12/Ti	Oxide	6.65	–	21.13	–	71.18	1.03	–
	Sulfide	6.02	–	19.44	–	62.61	0.61	11.3
FePMo-12/Ti	Oxide	6.88	0.27	23.13	–	69.73	–	–
	Sulfide	7.79	0.82	19.61	–	58.11	0.79	12.9
HPMo-6/Ti	Oxide	7.29	–	30.89	–	89.40	–	–
	Sulfide	7.02	–	29.50	–	82.13	0.26	11.3
FePMo-6/Ti	Oxide	4.96	0.41	22.36	–	71.92	–	–
	Sulfide	3.41	0.66	21.78	–	67.60	0.46	6.12

XPS spectra of P2p of the catalysts containing titania and iron reveal a large peak at 134.2 eV and a small peak at 129.3 eV (table 2). In accordance with [38], we can conclude that phosphorus $P2p_{3/2}$ with binding energy of 129.3 eV is associated with P bonded to Fe whereas phosphorus with binding energy of 134.2 eV corresponds to the surface PO_4^{-3} species. Formation of the Mo–P bond (table 2) is also not excluded [39–41].

A shift in the Ti2p binding energy up to $\sim$459.2 eV (observed in our HPMo-12/Ti and HPMo-6/Ti catalysts – see table 2) compared to that of the pure TiO_2 (458.0–458.8 eV) [42] indicates an interaction of TiO_2 with the loaded compound.

3.6.2. *Sulfides form*

XPS of the sulfided HPMo-12/Al catalyst reveals the presence of the $Mo3d_{5/2}$ with binding energy 228.9 eV which was assigned to Mo^{4+} ions [30,31,35] and small amount of unreduced Mo^{6+} ions in tetrahedral O-surrounding (232.6 and 233.7 eV). No Mo^{5+} ions are detected.

After sulfidation of both HPMo/Ti catalysts with 6 and 12 wt% Mo, the molybdenum surface concentration decreases (table 2). Curve fitting of the spectrum indicates that Mo^{6+} (Td) ions transforms into Mo^{5+} ions (231.1 eV) whereas Mo^{6+} (Oh) ions are transformed into Mo^{4+} ions (229.4 eV). In accordance with [34], some part of Mo^{6+} ions in sulfided HPMo/Ti catalysts remains in tetrahedral O-surrounding (233.1 eV). The Mo^{5+} peak appearing in the spectrum of the TiO_2-supported catalyst can be assigned to oxidic or oxysulfidic Mo species [43–45]. After sulfidation, the Ti2p binding energy does not change (459.2 eV).

Surface concentration of Mo in alumina-supported catalysts is low and the sulfidation of the catalysts leads to a further decrease in its surface concentration (table 2). Iron is absent practically on the catalyst surface after sulfidation. Phosphorus is found neither in the oxidic, nor in the sulfided alumina supported catalysts

3.6.3. *Sulfur state in the sulfided catalysts*

The TiO_2-supported catalysts show clear S2p doublet with binding energy of 162.6 and 163.4 eV whereas alumina supported catalysts show a large peak shifted to lower values of binding energy (table 2). The observed S2p binding energy (162.6 eV) corresponds to the presence of S^2-ligands in MoS_2 [43,44,46]. Some differences in binding energy of the first S2p peak observed at 161.8 eV with the HPMo-6/Ti catalyst and at 162.6 eV with HPMo-12/Ti indicate possibility of transient formation of S^{2-} ligand of MoS_x species at lower Mo concentrations [47]. The second part of the S2p spectrum with the value 163.9 eV (163.4 eV in our paper) has been assigned to sulfidation of titania [46]. However, the peak with 456.7 eV, ascribed to TiO_xS_y, is absent in our spectra. For that reason, we assign the S2p peak (163.4 eV) to S^{2-} or S_2^{2-} ligands [43,44].

Curves fitting of the Mo3d spectra of all sulfided catalysts detected the S2s peak with binding energy of 226.1–226.8 eV, which corresponds to S^{2-} [43]. Some difference in the width of the peaks of the alumina- and titania-supported catalysts can also observed: The S2s binding energy is higher for the titania-supported catalysts and it increases up to 227.0–227.1 eV after introduction of iron into the catalysts prepared on both supports.

4. Discussion

Results obtained in this paper show significant influence of a support and a promotor on the state of molybdenum in the HDS catalysts and on their activity in thiophene HDS.

Strong interaction between the loaded compound and a support leads to formation of the chemical compounds including the support ions. Presence of various surface compounds, (1. – Aluminum heteropolymolybdate; aluminum molybdate and aluminum phosphate on the alumina support; 2. – Anion of P (Ti) heteropolymolybdenum acid and oxomolybdates on the titania support), existence of which was confirmed by IR spectra, can explain different dispersion and state of molybdenum observed on titania- and alumina-supported catalysts.

Invariability of the Al–O bond value (74.9 eV) in the alumina-supported and of the Ti–O bond in the titania-supported catalysts can confirm additionally the formation of Al and Ti heteropolymolybdates in which heteroatom is surrounded with Mo ions.

High surface concentration of molybdenum, as well as a specific state of the active components can explain high activity of the catalyst prepared from heteropolycompound over TiO_2 (6 wt% Mo). It was explained by adsorption of the molybdenum species on the terminal OH-groups of the TiO_2, and thus, increased number of Ti–O–Mo bonds in the surface layer can be expected. Formation of the HTiMo acid and, particularly, preservation of the HPMo acid on the TiO_2 support surface could be a reason for the observed higher surface concentration of molybdenum and activity than those found in the alumina-supported catalysts. Theoretical composition of the considered surface compounds can be as follows: Heteropolyacid of Mo and Ti (observed on titania-supported catalyst) with Keggin structure gives ratio Mo/Ti(P) = 12. Contrary to this, Mo/Al value in aluminum heteropolymolybdate (observed on our alumina-supported catalysts) reaches the value 6. Supposing presence of such components on the catalysts surfaces, molybdenum concentration on the HPMo-12/Ti catalyst could be higher than that observed with HPMo-12/Al catalyst.

The slight growth of the activity on the alumina supported high-concentrated catalyst correlates with the H_2 consumption increase (table 1). A contrary to this result on the titania supported catalysts the high H_2 consumption is observed on the HPMo-12/Ti catalyst (table 1) and, at the same time, three times lower activity than that of HPMo-6/Ti. One can assume this founding is related to a higher accessibility of Mo species for hydrogen then for thiophene [48].

Curve-fitted spectra of Mo3d confirm higher concentration of Mo in octahedral coordination (Oh) in the TiO_2-supported catalysts (figure 5). The presence of Mo^{5+} ions, even in the oxidic form of the titania-supported catalysts contrary to alumina-supported ones, shows specific role of Ti ions in the active sites formation. Promoting role of TiO_2 itself can be expected due to the easy reduction of Ti^{4+} ions to Ti^{3+} ions, i.e. titania can be an electron promotor of Mo^{6+} ions transferring it into Mo^{5+} ions.

Various surface precursors lead to different extent of sulfidation with formation of S-containing species (XPS confirmed formation of oxysulfides, MoS_2 and MoS_x). Higher amount of sulfur in the TiO_2-supported catalysts can be related to easier reduction of Mo species (confirmed by TPR) as well as to their higher concentration on the TiO_2 surface. It is important to stress that the S/Mo ratio is always lower than value 2. This ratio is especially lower in those catalysts whose activity is higher. It is indirect evidence that oxysulfidic species of molybdenum are more active in HDS than sulfidic. The maximum HDS activity is observed when the optimum sulfur content is reached [49,50].

The effect of iron differs in dependence on the support used and molybdenum concentration. The significant promoting Fe influence is revealed in the low-concentrated 0.25FeMo-6/Al catalyst (figure 2) whereas at the high Mo concentration the activity increases quite little. The contrary Fe effect on the thiophene conversion is observed in the titania supported catalysts (figure 2).

In the alumina-supported catalyst, Fe is present in the bulk of the catalyst. Its promoting role in the alumina-supported catalysts is likely related to its higher ability to keep the surface Mo species in the Oh coordination after sulfidation (table 2). During sulfidation, the Mo surface concentration decreases with 30% on the HPMo-12/Al catalyst whereas in the 0.5FePMo-12/Al sample this Mo concentration decreases only with 12.8%.

Iron introduced as the FePMo salt in the TiO_2-supported catalysts, increases the Mo surface concentration, which grows during the sulfidation process (table 2). The Fe/Mo ratio sharply increases. Iron decreases the reduction of the molybdenum species:

- Mo^{5+} is absent in the calcined catalyst-XPS results
- H_2 consumption decreases.

In the TiO_2-supported catalysts, iron likely remains on the surface because it can substitute Mo in both anions, the loaded HPMo and the HTiMo formed during preparation of the catalysts:

$$FePMo_{12}O_{40} \rightarrow [P(Ti)Mo_{11}FeO_{39}] + MoO_4^{2-}$$

The presence of the band at ~674 cm^{-1} in the IR spectra of the TiO_2-supported catalysts confirms this assumption.

The increase in the surface Fe and P concentration and simultaneous decrease in Mo concentration over the 0.25FePMo-6/Ti catalyst could indicate formation of the Fe–P, Mo–P and/or Fe–P–Mo bonds after (H_2 + H_2S) pretreatment. Positive effect of phosphorus on the HDS activity can be related to easier sulfidation of the catalyst during the catalytic reaction [51].

5. Conclusions

The support has strong effect on the phase composition of catalyst precursors. Both the support and promotor play a very important role in the formation of the precursor active sites. The presence of P, Ti analogues of molybdenum heteropolyacid and oxymolybdates are revealed on the TiO_2 support, whereas aluminum heteropolymolybdate and aluminum molybdate arise on the Al_2O_3 support. XPS results show a higher concentration of both Mo^{6+} and Mo^{5+} species in the octahedral coordination over the TiO_2-supported than over alumina-supported catalyst. These species are precursors of the catalytic active sites.

The effect of iron differs in dependence on the support used and molybdenum concentration. The significant promoting Fe influence is revealed in the low-concentrated 0.25FeMo-6/Al catalyst whereas at the high Mo concentration the activity increases quite little. The contrary Fe effect on the thiophene conversion is observed in the titania supported catalysts. The TiO_2-supported catalyst with 6 wt% Mo shows nearly three times higher activity compared to that of the catalyst with 12 wt% Mo. In case the low molybdenum concentration the effect of iron is overlapped with promoting effect of titania. This result can be related to the multi-layer of Mo species formed in the catalysts with higher Mo concentration.

Formation of the Fe–P, Mo–P and FeMoP bonds after the sulfidation pretreatment is revealed in the XPS spectra on the TiO_2-supported catalysts.

References

[1] M. Rana, M.L. Huidobro, J. Ancheyta and M.T. Gomez, Catal. Today 107–108 (2005) 346.

[2] Y. Okamoto, M. Breysse, G. Murali Dhar and C. Song, Catal. Today 86 (2003) 1.

[3] G. Murali Dhar, S.M. Rana, K.S. Maity, N.B. Srinivas, R. Prasada Rao, C. Song, S. Hsu and I. Mochida (eds.), *Chemistry of Diesel Fuels*, Chapter 8 (Taylor&Francis, 2000).

[4] S. Damyanova, A. Spojakina and K. Jiratova, Appl. Catal. A: Gen. 125 (1995) 257.

[5] J. Ramirez, S. Fuentes, G. Diaz, M. Vrinat, M. Breysse and M. Lacroix, Appl. Catal. 52 (1989) 211.

[6] Y. Araki, K. Honna and H. Shimada, J. Catal. 207 (2002) 361.

[7] D. Wang, X. Li, E. Qian, A. Ishihara and T. Kabe, Appl. Catal. A: Gen. 238 (2003) 109.

[8] K.G. Groot, A.M. van der Kraan, V.H.J. de Beer and R. Prins, Bull. Soc. Chim. Belg. 93 (1984) 707.

[9] C.K. Groot, V.H.J. de Beer, R. Prins, M. Stolarski and W.S. Niedzwiedz, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 522.

[10] W.L.T.M. Ramselaar, V.H.J. de Beer and A.M. van der Kraan, Appl. Catal. A: Gen. 42 (1988) 153.

[11] W.L.T.M. Ramselaar, M.W.J. Craje, R.H. Hadders, E. Gerkema, V.H.J. de Beer and A.M. van der Kraan, Appl. Catal. 65 (1990) 69.

[12] A. Spojakina, N. Kostova, I. Yuchnovski, D. Shopov, T. Yurieva and T. Shochireva, Appl. Catal. 39 (1988) 333.

[13] A. Spojakina, S. Damyanova, D. Shopov, T. Shochireva and T. Yurieva, React. Kinet. Catal. Lett. 27 (1985) 333.

[14] A. Griboval, P. Blanchard, L. Gengembre, E. Payen, M. Furnier, L. Dubois and R. Bernard, J. Catal. 188 (1999) 102.

[15] J.-M. Tatibouet, C. Montalescot, K. Bruckman, J. Haber and M. Che, J. Catal. 169 (1997) 22.

[16] Ch. Kwak, M.Y. Kim, K. Choi and S.H. Moon, Appl. Catal. A: Gen. 185 (1999) 19.

[17] L.A. Santillán-Vallejo, J.A. Melo-Banda, A.I. Reyes de la Torre, G. Sandoval-Robles, J.M. Domınguez, A. Montesinos-Castellanos and J.A. de los Reyes-Heredia, Catal. Today 109 (2005) 33.

[18] A. Davidov and O. Goncharova, Usp. Khim. 62 (1993) 105.

[19] O. Solcova, D.Ch. Uecker, U. Steinike and K. Jiratova, Appl. Catal. A: Gen. 94 (1994) 153.

[20] H.J. Scofield, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 129.

[21] S.K. Maity, M.S. Rana, S.K. Bej, J. Ancheyta-Juarez, G. Murali Dhar and T.S.R. Prasada Rao, Appl. Catal. 205 (2001) 215.

[22] G.A. Zenkovets, V. Gavrilov, G. Kryukova, S. Tsybulya and V. Parmon, Kinet. Catal. 43 (2002) 621.

[23] Y. Araki, K. Honna and H. Shimada, J. Catal. 207 (2002) 361.

[24] D. Wang, X. Li, E. Qian, A. Ishihara and T. Kabe, Appl. Catal. A: Gen. 238 (2003) 109.

[25] A. Spojakina, S. Damyanova, Z. Vit and L. Petrov, Appl. Catal. 56 (1989) 163.

[26] E. Yurchenko, N.G. Kuskova and S. Batzanov, *LRS spectra of Inorganic Compounds*, (Novosibirsk, "Nauka", 1981).

[27] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1963).

[28] H. Jeziorowski and H. Knozinger, J. Phys. Chem. 83 (1979) 1116.

[29] Y. Iwasawa, Y. Nakamoto and S. Ogasawara, J. Chem. Soc. Faraday Trans. 74 (1978) 2968.

[30] M. Houalla, Ch. Kibby, L. Petrakis and D. Hercules, J. Catal. 83 (1983) 50.

[31] Y. Holl, R. Touroude, G. Maire, A. Muller, P. Engelhard and J. Grosmangin, J. Catal. 104 (1987) 202.

[32] R.I. Declerck-Grimee, P. Canesson, R.M. Friedman and J.J. Fripiat, J. Phys. Chem. 82 (1978) 885.

[33] A. Cimino and B. de Angelis, J. Catal. 36 (1975) 11.

[34] R. Quincy, M. Houalla, A. Proctor and D. Hercules, J. Phys. Chem. 94 (1990) 1520.

[35] D.S. Zingg, L.E. Makovsky, R.E. Tischer, F.R. Brown and D. Hercules, J. Phys. Chem. 84 (1980) 2898.

[36] M. Pope, *Heteropoly and Isopoly Oxometalates* (Springer-Verlag, Beer, 1983).

[37] P.J. Baltrus, R.J. Diehl, A.M. McDonald and F.M. Zarochak, Appl. Catal. 48 (1989) 199.

[38] D. Phillips, S. Sawhill, R. Self and M. Bussell, J. Catal. 207 (2002) 266.

[39] Y. Okamoto, Y. Nitta, T. Imanaka and S. Teranishi, J. Chem. Soc. (1982) 173.

[40] Y. Okamoto, K. Fukino, T. Imanaka and S. Teranishi, J. Catal. 74 (1982) 173.

[41] P. Perez-Romo, C. Potvin, J.M. Monoli, M. Chehimi and G. Djega-Mariadasson, J. Catal. 208 (2002) 187.

[42] R.L. Chin and D.M. Hercules, J. Phys. Chem. 86 (1982) 3079.

[43] Th. Weber, J.C. Muijsers, J.H.M.C. van Wolput, C.P.J. Verhagen and J.W. Niemantsverdriet, J. Phys.Chem. 100 (1996) 14144.

[44] Th. Weber, J.C. Muijsers and J.W. Niemantsverdriet, J. Phys. Chem. 99 (1995) 9194.

[45] J. Abart, E. Delgado, G. Erte, H. Jeziorowski, H. Knozinger, N. Tiele, X. Wang and E. Tagloaer, Appl. Catal. 2 (1982) 155.

[46] L. Coulier, J.A.R. van Veen and J. Niemantsverdiet, Catal. Lett. 79 (2002) 149.

[47] M. Thomas and I. Adams, J. Chem. Soc. Faraday Trans. 68 (1972) 755.

[48] A. Spojakina, E. Kraleva, K. Jiratova and L. Petrov, Appl. Catal. A: Gen. 288 (2005) 10.

[49] T.I. Koranyi, T. Szilagyi, I. Manninger and Z. Paal, Polyhedron 5 (1986) 225.

[50] T. Koltai, V. Galsan and P. Tetenyi, React. Kinet. Catal. Lett. 67 (1999) 391.

[51] J. Fierro, A. Lopez-Agudo, N. Esquivel and R. Lopez Cordero, Appl. Catal. 48 (1989) 353.