Catalysis Letters Vol. 110, Nos. 3–4, September 2006 (© 2006)
DOI: 10.1007/s10562-006-0110-2

Support effect on the formation of catalytic site precursors in the thiophene hydrodesulfurization

E. Kraleva,[a,]* A. Spojakina,[a] K. Jiratova,[b] and L. Petrov[a]

[a]*Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
[b]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic*

Received 25 May 2006; accepted 11 June 2006

The TiO_2 and Al_2O_3 supported FeMo catalysts (6 and 12 wt.% Mo) have been prepared using $(NH_4)_3Fe(OH)_6Mo_6O_{18}$ salt ($FeMo_6$). They have been studied by the IR, TPR, XPS and MS methods and tested in thiophene conversion. The initial salt transforms in analog of the TiMo acid anion on the titania support and alumina heteropolymolybdate anion on the alumina support. Higher thiophene conversion is observed on the TiO_2 supported catalysts.

KEY WORDS: TiO_2 and Al_2O_3 supports; ammonium ironheteropolymolybdate; thiophene conversion; IR; TPR; XPS; MS.

1. Introduction

The environmental protection is closely connected with better control of sulfur, nitrogen containing organic compounds and aromatic hydrocarbon emissions from petroleum derivatives into the air. The sulfur level in diesel fuels is expected to be lowered to 5–10 ppm by the end of 2010 in developed countries while in the USA the level of sulfur content will be limited to 15 ppm in 2006 [1, 2]. In order to meet the increasing ecological and economical regulations more attention is being paid to the use of catalysts having higher activity and selectivity. Nowadays the most widely used industrial catalysts are Co(Ni)Mo and NiW supported on alumina [1].

The hydrotreating activity of the catalysts depends on many factors that have not been still fully investigated. The improvement of these catalysts demands understanding of the active phase formation and their relation with the hydrodesulfurization activity. In spite of numerous studies of the support effect, there is no clear opinion on its participation in the formation and stabilization of active sites in the supported Co (Ni)–Mo (W) catalysts [3, 4]. The promotor role also retains not clear [5].

Recently the Mo(W) heteropoly compounds became very important starting material for the synthesis of catalysts [6]. It also was shown that those can be precursors of active sites in hydrodesulfurization catalysts [7, 8].

Heteropoly compounds can serve as a source of active components of hydrotreating catalysts. They contain both fundamental and promoting elements (heteropoly anion and countercation) in a single compound of defined structure, and therefore, their use in a study of HDS catalysts is valuable and can give useful information for further improvement of the catalysts.

An important role in providing of the optimal activity of catalysts plays the method of their preparation. It is known usage of different methods: impregnation, co-precipitation, sol–gel, mechanochemical treatment [9]. The impregnation of the support with the initial compounds is used in the synthesis of catalysts most often. It was shown the positive role of the mechanochemical treatment on the HDS catalysts activity [10, 11]. This method gives good results especially when a strong acid and base as of reagents realize the interaction [12].

The goal of this paper is to study the effect of the support (TiO_2 and Al_2O_3) and the active components (Mo and Fe) concentration on the phase composition and catalytic activity and selectivity in the thiophene hydrodesulfurization. The catalysts have been prepared by mechanochemical mixing of the FeMo heteropolycompound of Anderson type and support.

2. Experimental

2.1. Catalyst preparation

The samples have been prepared by mechanochemical mixing of the $(NH_4)_3Fe(OH)_6Mo_6O_{18}$ salt ($FeMo_6$) (Merck, pure) and the TiO_2 and Al_2O_3 supports in agate mortar during 1 h. The amount of the loaded salt was suitable to 6 and 12 wt.% Mo in catalysts. In the denotation of the samples, the number before Fe and after Mo means the wt.% concentration of corre-

---

*To whom correspondence should be addressed.
E-mail: kraleva@ic.bas.bg

sponding element. For example, the 0.6 FeMo6/Al sample contains 0.6 wt.% Fe and 6wt.% Mo supported on alumina. The component ratio Fe/Mo in the catalysts is suitable to its stoicheometric ratio in the FeMo salt.

The catalysts were dried 4 h at 105 °C and calcined 2 h at 350 °C. The catalysts are presented in table 1.

2.2. *Catalysts characterization*

The surface area of the catalysts was estimated from the nitrogen adsorption–desorption isotherms at −195 °C (BET method).

2.2.1. *TPR measurements*

TPR measurements were carried out in an apparatus described earlier [13]. Hydrogen/nitrogen mixture (10 mol.% H_2) was used to reduce catalysts at a flow rate of 17 $cm^3 \cdot min^{-1}$. The temperature was linearly raised at a rate of 20 °C min^{-1} up to 850 °C.

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 [14].

2.2.3. *XPS measurements*

XPS measurements were performed with an ESCALAB-Mk II (VG Scientific) electron spectrometer with a base pressure $1 \cdot 10^{-8}$ Pa. Samples were excited with MgKα radiation (hν = 1253.6 eV). The total energy resolution of the instrument was 1.2 eV as measured by half width (f.w.h.m.) of the Ag3$d_{5/2}$ photoelectron peak. Powdered samples were pressed into 12 mm-diameter stainless-steel sample holders to obtain a thickness of 0.7–1 mm. After introduction into the preparation chamber of the electron spectrometer, samples were evacuated to 10^{-6}–10^{-7} Pa, and transferred to the analysis chamber for XPS measurements. The glass reactor with sulfided sample was opened in a glove box connected to the fast entry lock of the XPS instrument. The sample was transferred to its holder without exposure to air. The following photoelectrons were recorded: C 1s, O 1s, Mo 3d, Ti 2p, Fe 2p and S 2p.

The binding energies (BE) of C 1s, O 1s, Mo 3d, Ti 2p, Fe 2p, and S 2p core electron levels were determined by computer fitting the measured spectra and were referenced to the C 1s XPS signal at 284.5 eV. The binding energies are estimated to be 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 [15].

2.2.4. *Moessbauer spectroscopy measurements (MS)*

The Moessbauer spectra were obtained at room temperature with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. A ^{57}Co/Cr (activity ≅20 mCi) source and the α-Fe standard were used. The experimentally obtained spectra were subjected to mathematical processing according to the least squares method. The parameters of hyperfine interaction such as isomeric shift (IS), quadrupole splitting (QS) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectra were determined.

2.3. *Catalytic activity*

Hydrodesulfurization of thiophene (HDS) was carried out in a continuous flow reactor at 623 K and atmospheric pressure. Each experiment was done with a fresh catalyst (0.1 g) that was standardized by in-situ calcination (30 min) in argon at 350 °C. Calcined catalyst was activated by sulfidation with a mixture of 10 vol.% $H_2S + 90$ vol.% H_2 during 1 h and 2 h at temperature 350 °C and flow rate 40 $cm^3 \cdot min^{-1}$to compare the activity after different time of sulfiding.

After activation had been completed, the catalyst was flushed (30 min) with argon at the same temperature, and then feeding the reaction mixture (6 mol.% of thiophene in hydrogen) with the thiophene WHSV 2 h^{-1}. Activity was calculated from thiophene conversion to hydrocarbons (C4).

Table 1
Catalyst samples and TPR data

Catalysts	S_{BET} ($m^2 \cdot g^{-1}$)	mmol H_2/g (20–650 °C)	mmol H_2/g (20–800 °C)	T_{max} (°C)
Al_2O_3	200	–	–	–
0.6FeMo6/Al	141	1.353	2.677	498; 788
1.2FeMo12/Al	110	1.429	2.822	502; 793
TiO_2	75	0.258	0.371	603
0.6FeMo6/Ti	53	2.147	3.473	514; 603; 773
1.2FeMo12/Ti	50	2.242	3.510	516; 603; 778

3. Results and discussions

In table 1 the catalysts and some of their properties are presented.

The support surface of the catalysts is about 30 % lower than that of the supports.

We suppose some reasons of the decrease in the specific surface area of the mechanochemically treated samples. It is the result of the local overheating of the supporting phase, its migration and blockage of the pores. The plastic deformation which the catalyst samples undergo during the mechanochemical treatment induce a number of non-steady-state processes, appearance of defects and/or destruction of the crystal lattice, variation in the form and the size of the particles, changes in the specific surface area and in the porosity [16, 17]. The energy accumulation in defects in the new phases increases the temperature and stimulates a transfer of the new phases in other ones with a lesser surface [16].

The high homogenization of the mixture of interacted components helps to mechanochemical synthesis. The hydration water separated from loaded heteropolycompound retains in the volume of the mixture [16] and most probably, has the important role in the new phases formation (specially, new heteropolycompounds). It was shown that mechanochemical synthesis proceeds easily when acid–base interaction can proceed [12, 16]. The sorption activity of the support increases [18, 19].

Along with high dispercity of the mixture the dense aggregates are formed during the mechanochemical treatment. These aggregates are inaccessible inside for the surface measure. Chemical composition of the catalysts affects the porous structure and surface. Probably the low concentration of components helps to be formed these dense aggregates [12].

Different phase composition can be seen in the figure 1.

In the IR spectrum of the initial salt $(NH_4)_3Fe(OH)_6Mo_6O_{18}$ the bands at about 944, 926, 890, 645, and 572 cm^{-1} characteristic of the Anderson type heteropolycompound are revealed.

The IR spectra of the TiO_2 supported catalysts are changed substantially in comparison to the initial salt. The principal bands at about 673, 910, 960, and 1060 $cm^{-1}$are appeared in the catalyst spectrum. The shifting of the ~943 cm^{-1} band observed in the initial salt to the value 960 cm^{-1} and the shoulder at about 1060 cm^{-1} in the new band appeared confirm a formation of new compound. Comparison of the detected bands with the characteristic bands of the TiMo HP acid at about 910; 960; 1060 cm^{-1}confirms the anion presence of this acid [20–22]. The band at ~1060 cm^{-1} is not detected clearly because of poor compensation of the support bands in this region. Very likely, it has a low intensity (low amount of the newly formed anion of the TiMo acid).

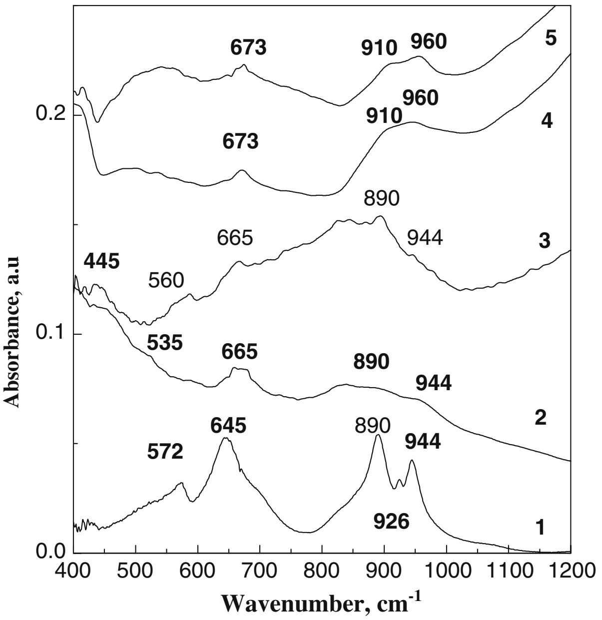

Figure 1. IR spectra of $(NH_4)_3Fe(OH)_6Mo_6O_{18}$salt-**1** and catalysts: 0.6FeMo6/Al-**2**; 1.2FeMo12/Al-**3**; 0.6FeMo6/Ti-**4**; 1.2FeMo12/Ti-**5**.

The band at ~673 cm^{-1} likely is related to a formation of the mixed TiMoFe(Ti) compounds as the result of the Mo substitution for Fe (Ti) in the TiMo anion [23].

The spectra of the alumina supported catalysts are similar to the spectrum of the initial salt. The bands at about 665; 445; 890; 944 cm^{-1} are characteristic of the bridge Mo–O–Mo and terminal M = O groups in the heteropolymolybdates of Anderson type [24]. We suggest formation of the $[AlMo_6O_{24}H_6]^{3-}$ anion analogue along with the preservation of the initial $FeMo_6$ salt anion because the first is formed easily as result of a strong interaction of molybdenum compound with alumina. The spectra of the Al and Fe heteropolyanions are similar. No bands at about 590, 880, 950, and 990 cm^{-1} characteristic of MoO_3 and $Al_2(MoO_4)_3$ in the alumina supported catalysts are revealed.

Thus, the effect of two supports as result of their interaction with the initial loaded compound is manifested in the formation of different heteropolycompounds on both, the Al_2O_3 and TiO_2 supports: the polymeric structure of Anderson type is observed (or is saved partially) on alumina and Keggin type one on titania.

Temperature programmed reduction of the catalysts revealed more intensive peaks for the titania supported catalyst in comparison to the alumina supported ones (not presented).

The TiO_2 supported catalysts shows higher H_2 consumption (table 1) in comparison to the Al_2O_3 supported ones and Tmax of the peaks are lower slightly.

The low temperature peaks (at 498–516 °C) in the profiles of the catalysts we relate to the more easily reducible molybdenum iones in the heteropolycompounds where Mo has the octahedral coordination. The presence of the initial and/or the new-formed heteropolycompounds was shown in the IR spectra of the samples (figure 1). The second enlarged high temperature peak (after 700 °C) shows further reduction of the formed products during experiment. This high temperature peak in the profile of the TiO_2 supported catalyst shows a shoulder at about 690 °C. It could be explained with the reduction of the iron titanates analog, of which components are reduced in the temperature region 600–650 °C [25]. Some amounts of the iron titanates could be formed during calcination of the catalysts [26]. The low intensive peak of the reduced TiO_2 support is appeared at 603 °C (table 1) [27].

The element states of oxidic and sulfided forms of the catalyst have been studied using XPS method.

The XPS and MS data are presented for the samples with 6 wt.% Mo only because no substantial difference in the spectra of the samples with various Mo concentration was observed.

The results for the $Mo3d_{5/2}$ XPS spectra are presented in the figure 2

The Mo^{6+} species in octahedral coordination with binding energy (b.e) of 232.5 eV (figure 2) appears in the spectrum of the TiO_2 and Al_2O_3 supported catalysts in oxidic form. It is in accord with the Mo state in the surface polymolybdate phases.

These XPS spectra change after sulfidation of catalysts. The spectrum of the titania supported catalysts sulfided 1 h reveals two doublets with binding energy 233.9 and 230.8 eV (figure 2). We suggest that the first doublet is related to Mo^{6+}(Td) and the second to Mo^{5+}. Very likely, Mo^{6+}(Td) is included in the iron molybdate phase while Mo^{5+} species are situated in the sulfided TiMo polymeric phase forming oxysulfides [27–30]. We suggest no MoS_2 phase formation after the catalyst sulfidation with the $H_2 + H_2S$ mixture during 1 h, because the XPS reveals no Mo^{4+}-iones,

The comparison of this XPS spectrum with the spectrum of the catalyst after reaction shows change in the Mo state. The spectrum fitting reveals two doublets with binding energy 228.3 eV and 230.1 eV. Most probably, the MoS_2 phase with Mo iones in the Mo^{4+} state is formed [27], and some amount of Mo^{5+} species retains in fully sulfided or/and the MoSx phase is present.

Sulfiding pretreatment of the titania supported catalysts during 2 h changes the XPS spectrum.

Deconvolution of the spectrum reveals three doublets with binding energy of 227.9, 229.0 and 230.9 eV. In agreement with [31, 32], we suggest that some Mo-species reduce in Mo^0, another lesser part reduces in Mo^{4+} included in the MoS_2 phase. The Mo^{5+}species revealed

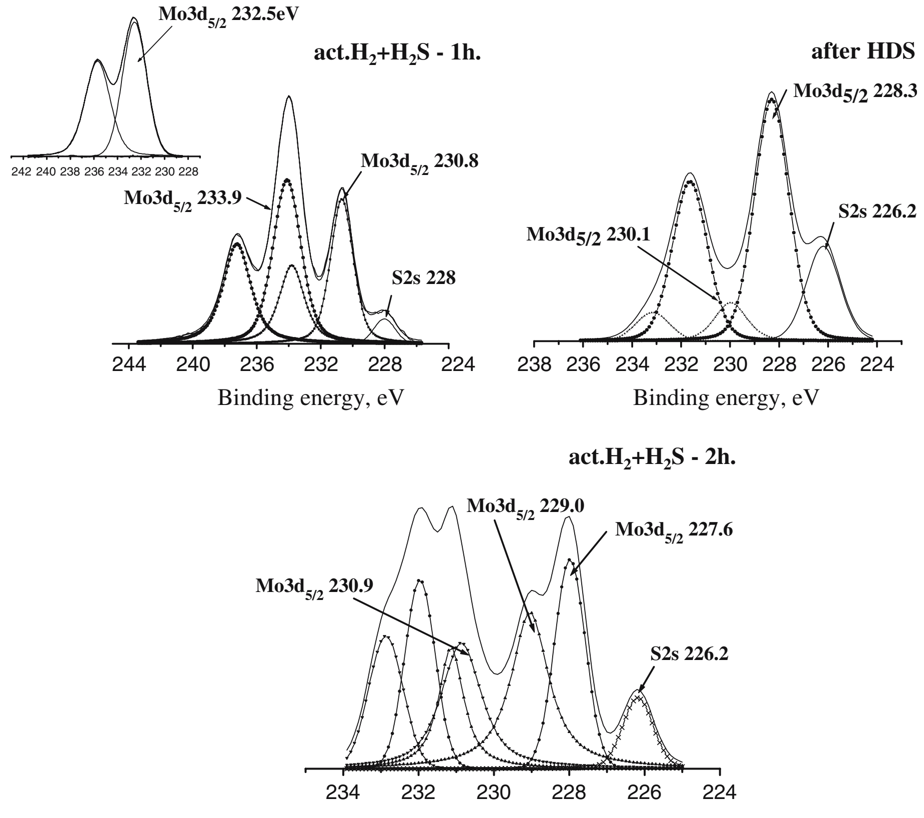

Figure 2. XPS spectra of the FeMo/Ti catalysts in oxidic and sulfided form: *Results are related with the samples of different concentration.

in the XPS spectrum are situated in the oxosulfided phase. These results show that a fuller reduction of Mo species is reached after a longer sulfidation.

In difference to the TiO_2 supported catalysts the Mo^{6+}(Oh) species in the alumina supported ones have been reduced after sulfidation in Mo^{4+} in the MoS_2 phase (figure 3). Binding energy of $Mo3d_{5/2}$ (229.5 eV) assigned to Mo^{4+} confirms this conclusion. Binding energy of the other doublet (232.2 eV) in the spectrum shows that some part of Mo^{6+}(Oh) does not change its state after sulfidation [27].

In the spectra of the sulfided catalysts the peak of S2s with binding energy 226.7 eV is revealed. It is described to S^{2-} appeared from adsorbed H_2S.

According to the XPS results the iron state in the oxidic and sulfided forms of the catalysts is related with Fe^{3+} (b.e. 709.7 eV) (the spectra are not presented).

Additional information about the iron state in the systems under investigation has been received from Moesbauer spectra (MS)

In table 2 the parameters of the MS spectra of the catalysts and initial salt are presented.

Moesbauer spectrum of the initial $(NH_4)_3Fe(OH)_6$-Mo_6O_{18} salt reveals superposition of overlapping lorencians. The results confirm the observed inlorence view. The width of the 2.39 $mm \cdot s^{-1}$ line is about 10 times greater than its natural width. The results could be explained if we suggest a presence of the Fe ions surrounded with ligands of different chemical nature (OH^- groups, ammonium ions, oxygen ions bonded with Fe and Mo).

Comparison of the spectra of initial salt and the titania supported catalysts reveals a change in the Fe ions state. In the catalyst spectrum the Fe ions in a high spin state and octahedral coordination are recorded. We suggest that they are in the state closed to one in the Fe^{3+} ions on oxygen coordination [33]. The spectrum treatment shows the ratio of two doublet components corresponding to the ultra disperse Fe species.

The MS pattern and its parameters for the alumina-supported catalysts are different from those of the initial $FeMo_6$ salt and the titania supported catalysts. The spectrum treatment is made using model with three doublets, two being assigned to Fe^{3+} ions in oxygen coordination and the third one to presence of iron in the initial salt or iron molybdate $Fe_2(MoO_4)_3$.

Hydrodesulfurization activity of the catalysts, related to one mol Mo, was evaluated from thiophene conversion (figure 4). It is seen that the TiO_2 supported catalysts are more active than the Al_2O_3 supported ones. The Mo concentration in the TiO_2 supported catalysts does not affect the activity. The FeMo salt anions are bound with the titania surface very strongly and the uniform monolayer coverage is reached. On the titania surface, Ti^{4+} ions are only octahedrally coordinated and the hydroxil groups are uniformly distributed, providing a homogeneous surface for adsorption of anions. When concentration of molybdenum increases up to 12 wt.%, the support surface is covered with a dense multi-layer. The thiophene molecule cannot reach lower layers of catalyst. The same activity of the high-concentrated catalyst can be explained by inaccessibility of Mo species to the thiophene molecules

In difference to the titania surface Al^{3+} ions on alumina are coordinated octahedrally or tetrahedrally and hydroxyl groups are formed preferentially in parallel raws. Aggregates formed from the particles of different sizes, combined in multi-layers, are also observed on the alumina surface with 12 wt. % Mo loading. Different phases in these catalysts including the volume iron molybdate $Fe_2(MoO_4)$ with a lower activity could explain a lower activity of the alumina supported catalysts. The HDS activity of the alumina supported catalyst increases at the higher Mo concentration, because the alumina higher surface has a higher surface and by this way is able to have more active sites.

The difference in the catalytic activity of the TiO_2 and Al_2O_3 supported samples also can be explained with a formation of different precursors of active sites and their concentration on the both of supports. The presence of polymolybdates in the catalysts leads to the easy reduction of Mo species. The Mo state however is different on the supports. As XPS results show in the TiO_2 supported catalysts, the Mo–O–Mo bonds of the newly

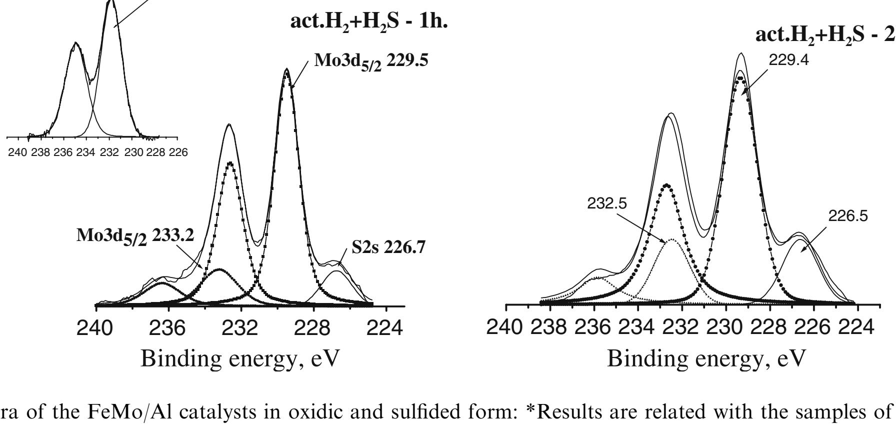

Figure 3. XPS spectra of the FeMo/Al catalysts in oxidic and sulfided form: *Results are related with the samples of different concentration.

Table 2
Parameters of Moessbauer spectra recorded with the catalysts

Catalysts	Components	IS ($mm \cdot s^{-1}$)	QS ($mm \cdot s^{-1}$)	FWHM ($mm \cdot s^{-1}$)	G (%)
$(NH_4)_3FeMo_6O_{24}.xH_2O$	Singlet	0.222	–	2.398	100
FeMo/Ti	Db1 core – Fe^{3+}	0.391	0.511	0.346	49
	Db2 shell – Fe^{3+}	0.352	0.794	0.806	51
FeMo/Al	Db1 core – Fe^{3+}	0.378	0.513	0.524	39
	Db2 shell – Fe^{3+}	0.352	0.912	0.607	32
	Db3 Fe^{3+}	0.417	0.180	0.349	29

*Results are related with the samples of different concentration.

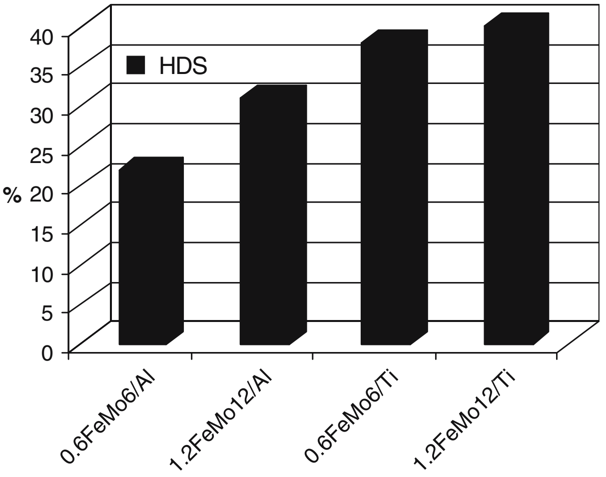

Figure 4. Thiophene conversion after 1 h sulfiding related to 1 mol Mo in catalysts.

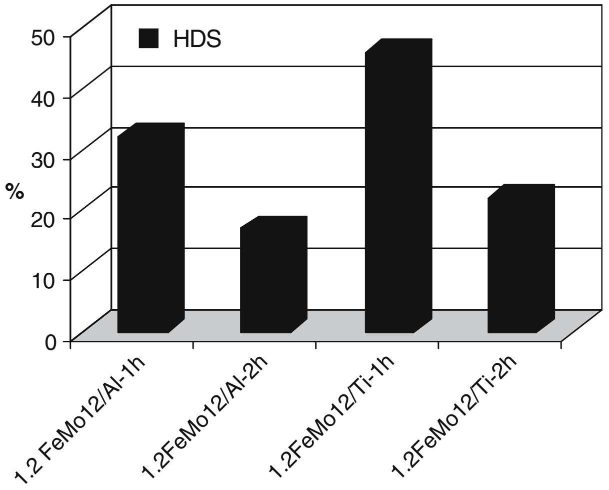

Figure 5. Thiophene conversion after 2 h sulfiding.

formed TiMo heteropolyacid are sulfided and the Mo^{5+} species in the oxosulfides occur in these catalysts (Mo–O–S bonds). A longer sulfidation leads to a formation of the MoS_2 phase (with Mo^{4+}) but a part of Mo^{5+} retains. Most probably it is present in the active sulfided phase.

HDS of the catalysts containing 12 wt. % Mo after 2 h activation is presented in figure 5.

The HDS activity of the catalyst, however, decreases two times (figure 5) when the Mo^{5+} ions quantity decreases. As can be seen the HDS activity decreases two times for catalysts supported on alumina and titania after a longer activation.

Promoting role of titanium in the TiMo acid formed can be expected due to the easy redox of $Ti^{4+} \leftrightarrow Ti^{3+}$ ions, i.e. titanium can be an electron promotor sustaining the Mo^{5+} iones presence in the catalysts. Presence of Mo^{5+}ions in the titania supported catalysts, observed even in the oxidic form of the catalysts, could confirm specific role of Ti ions in formation of the catalyst active sites.

In the difference to the TiO_2 supported catalysts in the sulfided alumina supported catalysts Mo^{6+} is reduced up to Mo^{4+} only, (XPS data). No Mo^{5+} species are observed and this could explain a lower activity of the alumina supported catalysts.

4. Conclusion

The results obtained show the principal role of the support in the precursor active phase formation and HDS activity of the catalysts.

In the studied FeMo containing catalysts a part the loaded iron heteropolymolybdate $(NH_4)_3Fe(OH)_6Mo_6O_{18}$ transforms into analog of the TiMo acid anion on the titania support. The corresponding alumina heteropolymolybdate analog is formed on the alumina support.

In the sulfided forms of the catalysts, Mo^{6+} and Mo^{5+} species are detected in the titania support whereas Mo^{6+} and Mo^{4+} species are revealed in the alumina one. HDS activity of the catalysts is related to the Mo^{5+}/Mo^{4+} ratio. Higher thiophene conversion is observed on the TiO_2 supported catalysts in comparison to the alumina supported ones. It is likely related to the presence of the Mo^{5+} species in the first of them.

Reduction of the Mo species in the TiO_2 supported catalyst in Mo^{4+} situated in the MoS_2 phase decreases the HDS activity two times.

Acknowledgments

The authors would like to thank Bulgarian and Czech Academy of Sciences for support the researches in the joint project.

References

[1] H. Topsoe, S.B. Clausen and E.F. Massoth, *Hydrotreating Catalysts, Science and Technology* (Springer, Berlin, 1996).
[2] K.G. Knudsen, B.H. Cooper and H. Topsoe, Appl. Catal. A 189 (1999) 205.
[3] J. Ramirez, L. Cedeno and G. Busca, J. Catal. 184 (1999) 59.
[4] J. Ramirez, S. Fuentes, G. Diaz, M. Vrinat, M. Breysse and M. Lacroix, Appl. Catal. 52 (1989) 211.
[5] G.K. Knudsen, B. Cooper and H. Topsoe, Appl. Catal. A: Gen. 189 (1999) 205.
[6] N. Mizuno and M. Misono, Chem. Rev. 98 (1998) 199.
[7] M.A. Maitra, W.N. Cant and L.D. Trimm, Appl. Catal. 48 (1989) 187.
[8] A. Spojakina, S. Damyanova and D. Shopov, React. Kinet. Catal. Lett. 27 (1985) 333.
[9] E. Gaffet, F. Bernard, J. Niepce, F. Charlot, C. Gras, G. Le Caer, J. Guichard, P. Delcroix, A. Mocellin and O. Tillement, J. Mater. Chem. 9 (1999) 305.
[10] S. Andonova, Ch. Vladov, B. Kunev, I. Mitov, G. Tyuliev, J.L.G. Fierro, S. Damyanova and L. Petrov, Appl. Catal. A: Gen. 298 (2005) 94.
[11] M. Kouzu, K. Uchida, Y. Kuriki and F. Ikazaki, Appl. Catal. A: Gen. 276 (2004) 241.
[12] G. Mestl and H. Knozinger, Langmuier 14 (1998) 3964.
[13] O. Solcova, D.Ch. Uecker, U. Steinike and K. Jiratova, Appl. Catal. A: Gen. 94 (1994) 153.
[14] A. Davidov and O. Goncharova, Usp. Khim. 62 (1993) 105.
[15] H.J. Scofield, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 129.
[16] V.V. Molcanov and R.A. Buianov, Usp. Khim. 69(5) (2000) 477.
[17] K. Ng and E. Gulari, J. Catal. 92 (1985) 340.
[18] R. Buianov and V. Molcanov, Chim. Promish. 3 (1996) 151.
[19] V. Molcanov, R. Buianov and V. Goidin, K&K, 39 (1998) 465 (rus.).
[20] O. Goncharova, A. Davidov, T. Yurieva and T. Shokhireva, React. Kinet. Catal. Lett. 20 (1982) 119.
[21] T. Shokhireva, T. Yurieva and G. Boreskov, React. Kinet. Catal. Lett. 19 (1982) 151.
[22] H. Jeziorowski and H. Knozinger, J. Phys. Chem. 83 (1979) 1116.
[23] E. Yurchenko, G.N. Kuskova and S.S. Bacanov, *LRS spectra of Inorganic Compounds* (Novosibirsk, Nauka, 1981).
[24] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1963).
[25] G.B. Raupp and J.A. Dumesic, J. Phys. Chem. 89 (1985) 5240.
[26] H.P. Stephens, R.G. Dosch and F.V. Stohl, Ind. Eng. Chem. Res. Dev. 24 (1985) 15.
[27] R. Quincy, M. Houalla, A. Proctor and D. Hercules, J. Phys. Chem. 94 (1990) 1520.
[28] 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.
[29] Th. Weber, J.C. Muijsers and J.W. Niemantsverdriet, J. Phys. Chem. 99 (1995) 9194.
[30] J. Abart, E. Delgado, G. Erte, H. Jeziorowski, H. Knozinger, N. Tiele, X. Wang and E. Tagloaer, Appl. Catal. 2 (1982) 155.
[31] D. Zingg, L. Makovsky, R. Tischer, F. Brown and D. Hercules, J. Phis. Chem 84 (1980) 2898.
[32] P.A. Spevack and N.S. McIntyre, J. Phis. Chem. 97 (1993) 11020 and 11031.
[33] W.L.T.M. Ramselaar, S.M.A.M. Bouwens, V.H.J. de Beer and A.M. van der Kraan, Hyperfine Interaction 46 (1989) 599.