EFFECT OF GAMMA IRRADIATION ON THE PROPERTIES OF MOLYBDENUM-CONTAINING CATALYSTS

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An effective method of modifying the catalytic properties of some oxide and sulfide catalysts is their pretreatment by γ-irradiation. Two types of Mo-containing catalysts were irradiated and changes in physico-chemical properties were studied. Alumina and silica were used as supports for catalysts. After irradiation of the catalyst support a signal appears at g=2.00 in the ESR spectrum, ascribed to presence of defects in the crystal lattice. The γ-irradiation pretreatment of samples leads to considerable modification of their bulk and surface structure and consequently changes in their adsorption and catalytic properties. The γ-irradiation stabilizes and slightly increase the thiophene conversion on the H_2 and H_2S pre-treated Mo/γ-Al_2O_3 sample in comparison with non-irradiated one. The γ-irradiation of the Mo/SiO_2 sample leads to lower but the steady state activity independently from H_2 or H_2S pre-treatment.

1. Introduction

Structural and phase transformations in solids under irradiation have been a subject of intensive investigation. [1-3]. The radiation induced transformation is a multiparameter process, which depends on the radiation dose and the microstructure and chemical composition of irradiated solids. The properties of the catalysts can be modified by the method of their preparation as well as during different stages of their usage. One of the methods for catalyst modification is the irradiation treatment [3-8]. Irradiation enhanced sintering, removed a considerable fraction of surface acidity. The cracking process of n-hexadecane was significantly accelerated by γ–irradiation. The radiation effect will not be so efficient at very high cracking temperature where thermolytic C-C bond dissociation occurs. The phase composition of the catalysts depends on the support used. Its influence is determined by its point of zero charge.

The ESR method is based on energy absorbance by samples possessing electrons with unpaired spins, upon introducing the samples in a magnetic field. The systems, containing molybdenum, are among the most intensively studied objects, starting as early as the 1960s [9]. Analysis of the ESR spectra offers a direct approach to the determination of symmetry and electronic structure of the centers concerned [10]. This technique is very sensitive and allows detection of very small concentration of paramagnetic sites. The aim of this paper is to study the effect of γ-irradiation on the catalytic properties and structure of the alumina and silica-supported catalysts prepared using 12-molybdophosphoric heteropoly acid as source of molybdenum.

2. Experimental

2.1. Samples Preparation

γ-Al_2O_3 (S_{BET} = 220 m^2g^{-1}) and SiO_2 (S_{BET} = 175 m^2g^{-1}) were used as supports. The samples of the catalysts were prepared by incipient wetness impregnation of alumina or silica with aqueous

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solution of 12-molybdophosphoric heteropoly acid (HPMo). The molybdenum content was 12 wt. %. The samples were dried at 343 K for 4 h and calcined at 623 K for 2 h. Gamma irradiation of the samples was carried out using ^{60}Co as a source. Irradiation was performed on the oxidic form of the catalysts prior to their reduction and sulfidation. All the irradiation runs were performed in air at room temperature and atmospheric pressure. Irradiation inside the bulk of the sample ensured about 95 % homogeneity of the absorbed dose. The total dose of sample irradiation was 500 kGy.

2.2. Samples characterization

The IR spectra were recorded on a Bruker IFS-25 Fourier Transform IR spectrometer using potassium bromide pellets. Compensation of absorption from the support was used in the 400- 1500 cm^{-1} range by subtracting the normalized spectrum of equivalent support amount from the spectra of the samples.

Temperature-programmed reduction (TPR) measurements were carried out by hydrogen-argon mixture (10 % H$_2$) with a flow rate of 40 ml min^{-1}. The temperature was linearly raised at rate 20 K min^{-1} up to 1000 K.

The electron spin resonance (ESR) spectra were acquired on a Bruker 200 D spectrometer at room temperature in the 0-5000 Gs range. All spectra were acquired under similar condition. Prior to recording, the samples were treated in a quartz reactor with flow of hydrogen sulfide or hydrogen-thiophene mixture at 623 K.

The catalytic activity of the samples was tested in model reaction hydrodesulfurization (HDS) of thiophene in a flow system at atmospheric pressure, temperature 623 – 673 K and space velocity of 0.6 – 1.6 h^{-1} with gas chromatographic analysis of products. Before measurement of the HDS activity two methods of activation of the samples were applied: (i) reduction of the samples by H$_2$ at 623 K and (ii) H$_2$S treatment at 623 K. The catalysts were pretreated in situ under dry argon flow until the reaction temperature was reached and then were held at this temperature under hydrogen-sulfide flow (40 ml min^{-1}) for 0.5 h. The physically adsorbed hydrogen sulfide was purged with argon.

3. Results and discussion

The IR spectra of the catalysts and model compounds are represented in Fig 1. The characteristic band of the initial 12-molybdophosphoric heteropoly acid (780, 860 960 cm^{-1}) along with the bands characteristic for MoO$_3$ (820, 860, 990 cm^{-1}) are revealed in the spectrum of non-irradiated Mo/SiO$_2$ catalyst. The molybdena content slightly increases after γ-irradiation of the sample Mo/SiO$_2$.
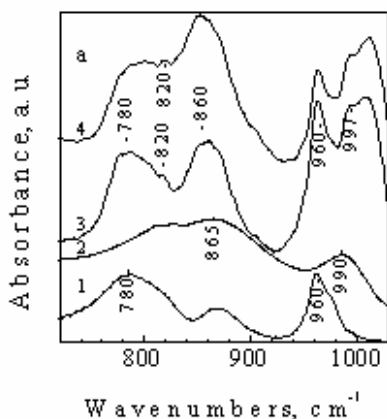

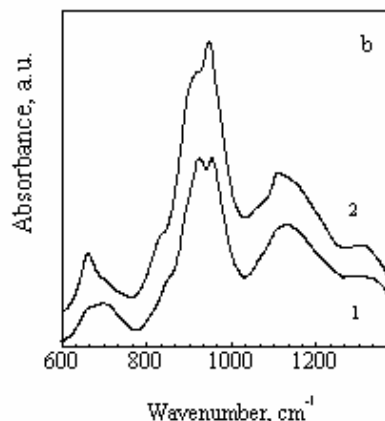Fig. 1a. IR spectra of initial HPMo (1), MoO$_3$ (2), and catalysts initial Mo/SiO$_2$ (3), irradiated Mo/SiO$_2$ (4)

Fig. 1b. IR spectra of catalysts: initial Mo/γ-Al$_2$O$_3$ (1), irradiated Mo/γ-Al$_2$O$_3$ (2)

The IR spectrum of the non-irradiated sample Mo/γ-Al$_2$O$_3$ reveals a strong interaction of the initial HPMo with the γ-Al$_2$O$_3$ (Fig. 1 b). The band at 890 cm^{-1} characteristic for tetrahedral molybdenum (Mo Td) in the deformed MoO$_4^{2-}$ anion appears. The initial HPMo destroys and analog of [AlMo$_6$O$_{24}$]$^{3-}$ with a lower polymerization degree forms. A large band at about 1120 cm^{-1} reveals the AlPO$_4$ surface phase formation. In the spectrum of irradiated sample Mo/γ-Al$_2$O$_3$ (Fig. 1b – curve 1) is observed an increase in the intensity of the band at 948 cm^{-1} characteristic for Mo-O-bonds in octacoordinated (Mo Oh) molybdenum structures. In addition, the shoulder at 1050 cm^{-1}, characteristic of the PO$_4$ tetrahedra is better expressed in the spectrum of the irradiated sample (Fig. 1b – curve 2).

TPR data of the catalysts are shown in Table 1. TPR patterns of all catalysts are similar, since they consist of two main reduction peaks. The supports SiO$_2$ and γ-Al$_2$O$_3$ undergo no reduction in the temperature region under investigation. The reduction of polymolybdate Mo^{6+} species to Mo^{4+} gives a reduction peak with maximum at 500-590 $^{\circ}$C, whereas the reduction peak with maximum above 650 $^{\circ}$C has been related to further reduction steps of molybdenum [11].

Table 1. Temperature programmed reduction patterns of the catalysts.

Sample	Tmax, $^{\circ}$C		MmolH$_2$g$_{cat}^{-1}$
	1	2	
Mo/γ-Al$_2$O$_3$	505	743	1.26
Mo/γ-Al$_2$O$_3$ irradiated	512	776	1.33
Mo/SiO$_2$	590	780	0.91
Mo/SiO$_2$ irradiated	560	772	1.09

Fig. 2 shows the TPR profile of the irradiated Mo/SiO$_2$ catalyst as example. The shift of the main TPR peak toward lower temperature after irradiation of the Mo/SiO$_2$ sample could be attributed to the formation of Mo species with higher dispersion. TPR results have shown that the reducibility of the samples changes in the order:
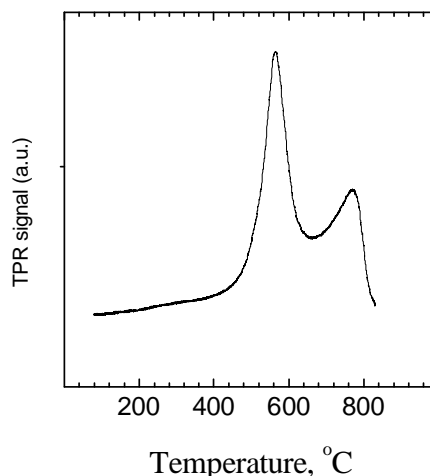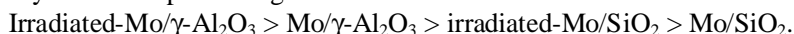
Irradiated-Mo/γ-Al$_2$O$_3$ > Mo/γ-Al$_2$O$_3$ > irradiated-Mo/SiO$_2$ > Mo/SiO$_2$.

Fig. 2. TPR profile of the irradiated catalyst Mo/SiO$_2$

The reduced samples reveal a lower HDS then presulfided ones independently from the used support. Sulfidation of the irradiated samples with hydrogen sulfide evolved during reaction changes the bond of molybdenum with sulfur. Probably by this way irradiation activates and stabilizes the active sites for hydrodesulfurization. The irradiation increases and stabilizes the thiophene conversion of the pre-reduced sample Mo/γ-Al$_2$O$_3$. Favorable effect of the pretreatment by hydrogen sulfide is better expressed in the sample Mo/SiO$_2$ in comparison with Mo/γ-Al$_2$O$_3$. The irradiation

stabilizes and slightly increases the thiophene conversion on the pre-reduced and pre-sulfided Mo/γ-Al$_2$O$_3$ sample in comparison with non-irradiated one. It has been shown that γ-Al$_2$O$_3$ possesses relatively high radiation-catalytic properties which most probably affect the molybdenum state in catalyst [8]. The γ-irradiation of the Mo/SiO$_2$ sample leads to a lower but the steady-state activity independently from H$_2$ or H$_2$S pre-treatment. The high selectivity towards n-butane of pre-sulfided Mo/SiO$_2$ sample decreases after irradiation. The observed results show that the γ-irradiation leads to changes in the interaction between hydrogen sulfide and the precursor of the catalytic active sites.

Table 2. Catalytic properties of the samples.

Sample	Thiophene conversion	Selectivity to butane
Pre-reduced Mo/γ-Al$_2$O$_3$ [a]	15	20
Pre-reduced irradiated Mo/γ-Al$_2$O$_3$ [a]	24	24
Pre-sulfided Mo/γ-Al$_2$O$_3$ [a]	27	21
Pre-sulfided irradiated Mo/γ-Al$_2$O$_3$ [a]	29	24
Pre-reduced Mo/SiO$_2$ [b]	20	17
Pre-reduced irradiated Mo/SiO$_2$ [b]	15	14
Pre-sulfided Mo/SiO$_2$ [b]	49	33
Pre-sulfided irradiated Mo/SiO$_2$. [b]	33	22

[a] space velocity 1.6 h^{-1};
[b] space velocity 0.8 h^{-1}

ESR spectroscopy was widely used and proved to be very informative for detailed characterization of reduced Mo-species [11-18]. The structure of signal gives information about the coordination of the species. It is very sensitive to small concentrations. One electron redox process on the Mo/SiO$_2$ surface was confirmed and monitored directly by ESR. Figs. 3 a and b represent the typical experimental spectra of Mo/γ-Al$_2$O$_3$ and Mo/SiO$_2$, respectively. Molybdenum with degree of oxidation Mo^{6+} (d^{o}) is diamagnetic and for this reason it does not given any ESR signal. The ESR signals, registered with Mo-containing catalysts, are attributed to Mo^{5+} (d^{1}).
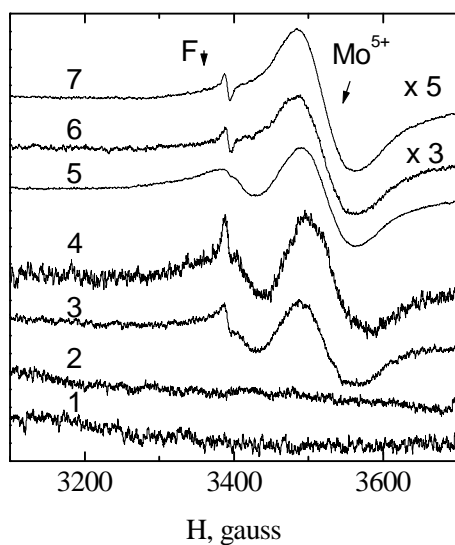

Fig. 3a. ESR spectra of support Al$_2$O$_3$ and Mo/Al$_2$O$_3$ catalysts: 1 – support Al$_2$O$_3$; 2 – irradiated support Al$_2$O$_3$; 3 – irradiated catalyst Mo/Al$_2$O$_3$; 4 – irradiated and pre-sulfided catalyst; 5 – pre-sulfided catalyst after HDS; 6 – irradiated presulfided catalyst Mo/Al$_2$O$_3$ after HDS; 7 – irradiated catalyst Mo/Al$_2$O$_3$ after HDS.
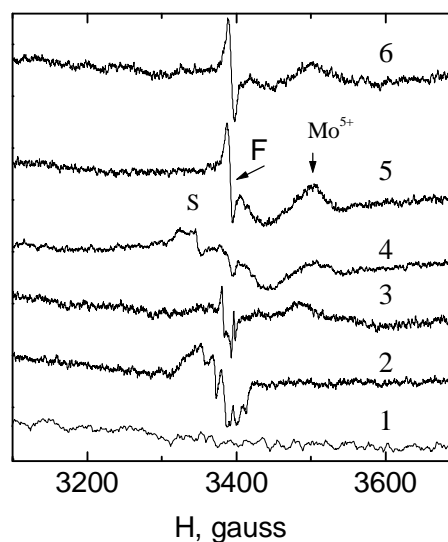
Fig. 3b. ESR spectra of support SiO$_2$ and Mo/SiO$_2$ catalysts: 1 – support SiO$_2$; 2 – irradiated support SiO$_2$; 3 – irradiated catalyst Mo/SiO$_2$; 4 – irradiated and pre-sulfided catalyst; 5 – pre-sulfided catalyst after HDS; 6 – irradiated presulfided catalyst Mo/SiO$_2$ after HDS.

The ESR spectra of the Mo-containing catalysts show considerable variations depending on the nature of support and on the method of preliminary treatment (Fig. 3). The initial and irradiated support γ-Al_2O_3 gave no ESR signals (Fig. 3a, curves 1 and 2). In contrast to the irradiated SiO_2 support posses the ESR signal (Fig 3b, curve 2) associated to formation of radical centers.

$$\equiv Si\text{-}O\text{-}Si\equiv \quad\quad \rightarrow \quad\quad \equiv Si\bullet \quad + \quad\quad \equiv SiO\bullet$$

These radicals interact with oxygen from molybdenum surrounding:

$$\equiv Si\bullet \quad + \quad O=Mo=O \quad \rightarrow \quad\quad \equiv Si\text{-}O\text{-}Mo=O$$
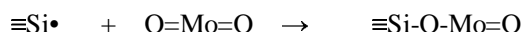
The nature of the support is of great importance. The silica does not stabilize Mo^{5+}, while alumina stabilizes it. A weak symmetric signal with a long trailing tail has been registered in the irradiated Mo/γ-Al_2O_3 catalyst, possessing an average value of the g factor 1.93, ascribed to molybdenum in the form of oxo-Mo^{5+} ions (Fig. 3 a, curve 3). The appearance of this signal in the deposited system Mo/γ-Al_2O_3 is attributed to the occurring interaction between the molybdenum and the support. The irradiated Mo/SiO_2 sample shows an asymmetric signal (Fig.3 b, curve 4) with g-tensor components $g\perp = 1.940$ and $g\| = 1.880$. This ESR signal has been ascribed to the Mo^{5+} ions surrounded by oxygen ligands occurring in distorded octahedral coordination with the shortest molybdenyl bond Mo=O.

Various signals are registered in the ESR spectra of the irradiated and pre-sulfided Mo/SiO_2 sample. The intensity of the signal of Mo^{5+} in a mixed O,S-surrounding with $g\| = 2.029$ and $g\perp = 1.998$ is low (Fig, 3b, curve 4). The signal registered around g = 2.000 is due to the available paramagnetic sulfur, present in polyatomic sulfur radicals [12-15]. The signal can be a triplet one (Mo/SiO_2) or singlet one (Mo/γ-Al_2O_3), depending on the support. The observed singlet with g = 2.050 in the spectrum of presulfided Mo/γ-Al_2O_3 sample after thiophene hydrodesulfurization (Fig. 3a, curve 5) could be assigned to bulk phase defects in a MoS_2-like phase [16]. The second signal in this spectrum is an intensive isotropic signal at about g = 1.930 characterizes the availability of oxo-Mo^{5+} ions. Most likely the signal at g = 2.004 is ascribed to the occurrence of defects, probably *F* centers, in the crystal lattice [8].

Two signals denoted, $g_1=1.94$ and $g_2=1.99$, are registered after conducting the catalytic test of the studied Mo-containing samples. The first one characterizes the presence of oxo-Mo^{5+} ions of structures, available in the calcined precursor. The second signal characterizes both the presence of Mo5+ ions in O, S-surrounding, owing to the partial substitution of oxygen with sulfur, as well as the presence of paramagnetic sulfur. A widening of the second signal to towards lower fields is observed in the spectra of the samples after carrying out the catalytic test.

4. Conclusions

The phase composition of the catalysts depends on the supports used. Strongly adsorbed species of HPMo on the silica and a mixture of tetrahedral molybdate, aluminium heteropolymolybdate with octahedral molybdenum and phosphate are revealed in the IR spectra of Mo/γ-Al_2O_3 catalyst. After γ-irradiation no meaningful changes in the spectrum of Mo/SiO_2 sample are marked whereas Mo(Oh) amount in the Al_2O_3 supported one rises simultaneously with decrease of the Mo(Td).

ESR results suggested the presence of Mo^{5+} in the irradiated samples and paramagnetic sulfur in the form of polyatomic sulfur radicals in pre-sulfided samples.

The irradiation alters the reducibility of the samples and in that way influences their hydrodesulfurization activity.

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