

An application of Mössbauer spectroscopy in the studies of iron-molybdenum silica mesoporous materials

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Abstract. Iron-molybdenum silica mesoporous materials were obtained by the application of direct hydrothermal method. Four samples with different metal contents relative to silica were investigated. Incorporation of iron and molybdenum ions in the synthesis stage led to structural changes of the MCM-41 support. With an increasing metals content, cylindrical pores of silica initially transformed into bottle-neck type pores, and then into the slit-like ones. Mössbauer spectroscopy investigations indicated that Fe ions were embedded in the silica walls and then formed nanosized crystallites in the pores. Superparamagnetic phase was observed at liquid nitrogen temperature.

Key words: iron • MCM-41 porous silica • molybdenum • Mössbauer effect • superparamagnetic nanoparticles

Introduction

Iron-molybdenum oxide systems show interesting structural and magnetic properties. They have found wide applications as catalysts in the reactions of selective oxidations, mainly methanol to formaldehyde [8] and alkylaromatics to suitable aldehydes or acids [1, 2]. The decrease of activity and increase of selectivity relative to the total oxidation products have been ascribed to the transformation of the structure of catalysts, related with the formation of volatile molybdenum oxide and iron-rich surface oxide phases [1, 2, 5, 8]. One of the directions of the development of catalysts is the preparation of nanosized or strongly dispersed $\text{Fe}_2(\text{MoO}_4)_3$ - MoO_3 phases on the suitable supports.

Condensation of silica around self-assembled surfactant molecules or modification of layered silicates are the main routes for preparation of silica mesoporous materials with a highly ordered porous structure and a large surface area, extending 1000 m^2/g . Simultaneous introduction of iron or molybdenum salts into the silica synthesis mixture can facilitate formation and stabilization of nanometre oxide species. However, the presence of iron or molybdenum ions may induce distortion of high symmetry of the micelles and thus contribute to the structural changes of materials.

Mössbauer spectroscopy is a powerful tool for investigation of the small iron oxide species in the supported and unsupported systems. The changes of the values of hyperfine interactions parameters may reveal the nature of interactions between iron, molybdenum and silica support. It has been demonstrated that the structural properties of the silica mesoporous materials may influence location, redox, magnetic properties and

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Table 1. Metal concentration, structural and surface properties of the samples. S_{BET} – specific surface area, V_t – BJH cumulative adsorption pore volume of pores, w_d – average pore diameter by BET

Sample	Assumed metal concentration (wt.%)		S_{BET} (m ² /g)	V_t (cm ³ /g)	w_d (nm)
	Fe	Mo			
Fe-Mo(A)-Si	3	1.1	1133.0	0.9	3.5
Fe-Mo(B)-Si	6.5	2.2	1051.4	1.0	3.4
Fe-Mo(C)-Si	12.5	4.2	817.7	1.1	6.1
Fe-Mo(D)-Si	24.3	8.2	472.9	1.0	9.5

a valence state of iron species. The intrinsic finite-size effects induce relaxation phenomena in the nanoparticles with high contributions of superparamagnetic component [10].

The aim of the studies was elucidation of the influence of metal ions concentration on the structural, surface and redox properties of iron-molybdenum silica materials. The magnetic nature of oxide species was investigated by the application of Mössbauer spectroscopy.

Experimental

Iron-molybdenum silica mesoporous materials were obtained by the application of direct hydrothermal method. Hexadecyltrimethylammonium bromide surfactant was dissolved in distilled water, then suitable amounts of iron nitrate and ammonium heptamolybdate salts were introduced. Next tetraethylorthosilicate (TEOS) was slowly added to the mixture during stirring. The pH of the solution was slowly increased by the introduction of ammonium hydroxide. The mixture was stirred for 1 h. The obtained product was filtered, washed with distilled water, dried overnight at 90°C and calcined in air at 550°C for 6 h in order to remove surfactants and transformation of precursors. Molar ratio of iron to molybdenum was the same in all samples, Fe/Mo = 2/3. The introduced amounts of iron were varied, in order to obtain samples containing from 3 wt.% (denoted as Fe-Mo(A)-Si) to 24.3 wt.% (for Fe-Mo(D)-Si) (Table 1).

The porous structure of materials was determined by the analysis of the nitrogen adsorption/desorption isotherms obtained volumetrically at –196°C using an ASAP 2405N apparatus (Micromeritics Corp., USA). Samples before measurements were outgassed (under ~10² Pa) at 200°C. The adsorption data were used to evaluate BET (Brunauer-Emmet-Teller) specific surface area, S_{BET} (from the linear BET plots). The mesoporous structure was characterized by the distribution function of mesopore volume calculated by applying the Barrett-Joyner-Halenda (BJH) method.

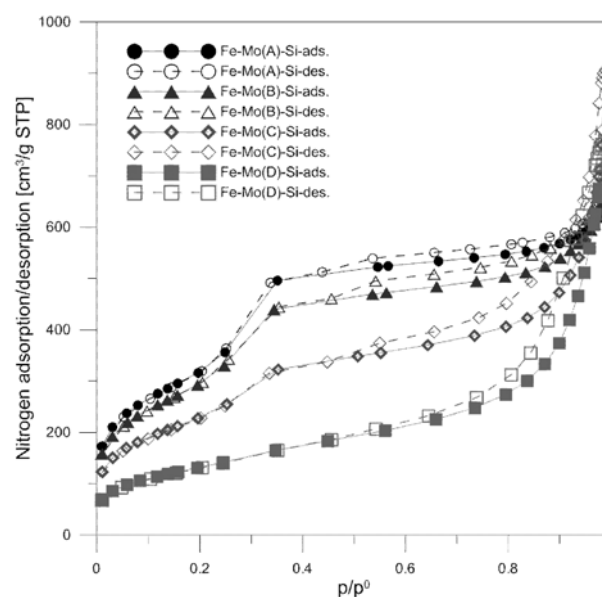
Temperature-programmed reduction (TPR) studies were performed in the AMI-1 apparatus (Altamira Instruments Inc.). The samples were heated up in a hydrogen/argon mixture (with total flow rate 30 ml/min). The temperature was increased with the rate 10°C/min. Water was removed from the stream (prior the TCD) in a cold trap with an LN₂-methanol mixture.

Mössbauer spectra were recorded using a constant acceleration spectrometer with a ⁵⁷Co(Rh) source at room and LN₂ temperatures. The isomer shift, δ , was calibrated against a metallic iron foil at room temperature.

Results

The porous structure and surface properties of the materials modified with small amounts of iron and molybdenum (samples Fe-Mo(A)-Si and Fe-Mo(D)-Si) were similar to the MCM-41 pure silica mesoporous supports. Samples showed a large surface area (S_{BET}) extending 1000 m²/g (Table 1). The shape of the adsorption/desorption isotherms as a function of p/p_0 , where p_0 is the saturation pressure, indicated the formation of regular mesopores with a mean pore diameter (w_d) of 3.5 nm (Fig. 1). A small and flat hysteresis loop can be observed in the range of relative pressures ranging from 0.5 to 0.9 of p/p_0 . This effect can indicate the presence of some irregularities in the structure of silica mesoporous material, connected with the development of bottle-neck type pores.

An increase of metal concentration induces distortion of the well-ordered structure and decrease the total surface area of the samples. A typical step on the isotherms at $p/p_0 = 0.3$ becomes less pronounced, and finally disappears for the Fe-Mo(D)-Si sample (Fig. 1). Simultaneously, the hysteresis loop at higher relative pressures is developed and is shifted to higher relative pressures (Fig. 1). These effects result from the transformation of the regular channels into the worm-like type, with more open structures and formation of macropores. The shape of the isotherm for the Fe-Mo(D)-Si may indicate the presence of slit-like pores, which probably resulted from condensation of silica and deposition of oxides in the lamellar bilayer phases of surfactants. In our opinion

**Fig. 1.** Nitrogen adsorption/desorption isotherms, p/p_0 , where p_0 is the saturation pressure.

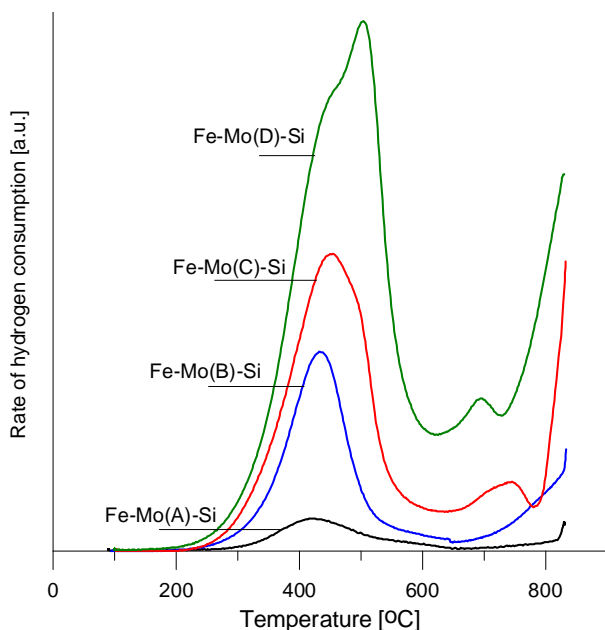
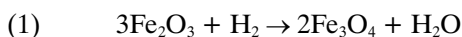


Fig. 2. TPR curves of iron-molybdenum silica modified oxide systems.

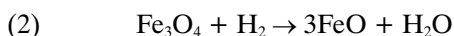
such effects are connected with distortion of the micellar structures of surfactant molecules caused by the introduction of large amounts of iron and molybdenum ionic species and their transformation into the oxide nanoparticles located in the as-prepared silica pores and embedded within the silica walls. It has been often reported that precipitation of iron and molybdenum oxides at relatively high values of pH of the solution in the presence of surfactants can lead to the formation of layered oxides of different structures [4, 9, 12].

Strongly dispersed iron and molybdenum oxide species, with the size below detection limit of the method may be evidenced in the X-ray diffraction studies [3].

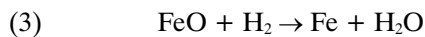
TPR curves of iron-molybdenum silica modified oxide systems are shown in Fig. 2. Reduction of the oxide phases revealed by TPR studies starts at low temperatures, at about 200°C. The first reduction maximum in the samples containing small amounts of modifiers is observed in the range of 200–600°C. The second maximum begins at higher temperatures. The intensity of the first reduction maximum increases with an increase of iron and molybdenum content. The definite assignments of maxima to the reduction of particular oxide species in the supported systems may always bring some uncertainties without application of the additional techniques. In many supported systems only one broad low-temperature maximum has been observed. The lowest part of maximum on the TPR curves is usually anticipated as the reduction of free Fe_2O_3 , according to the reaction equation:



Reduction of Fe_2O_3 species interacted with support usually occurs at higher temperatures. In the second stage the Fe_3O_4 phases are reduced as follows:

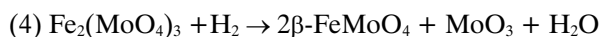


Reduction of FeO usually occurs at a temperatures of above 700°C according to the equation:



The structure of molybdenum oxides depends on the concentration and metal-support interactions. They can be present in the form of small isolated species, layered structures and large oxide particles. During reduction, stepwise routes are also usually observed.

The interpretation of the course of TPR curves for iron-molybdenum systems is even more complicated due to the fact that the materials are composed not only of the individual iron and molybdenum oxide phases, but they exhibit mutual interactions and may form chemical compounds. Iron molybdate are initially reduced and decomposed to the molybdenum oxides MoO_3 or Mo_4O_{11} :



Molybdenum oxide MoO_3 is then initially reduced to MoO_2 , and next to the metallic molybdenum at high temperatures. $\beta\text{-FeMoO}_4$ is successively reduced, through FeMoO_3 , $\text{Fe}_2\text{Mo}_3\text{O}_8$ and Fe_3O_4 , and oxides in the lower oxidation states. Finally, mixed crystals of metallic iron, molybdenum and intermetallic compounds Fe_3Mo are formed [6]. In the case of silica supported systems, high reduction temperature may also facilitate the formation of different iron silicalites of low reducibility.

Mössbauer studies were performed in order to determine some magnetic properties of the iron-molybdenum silica mesoporous materials. Mössbauer spectra of all the studied samples measured at room temperature (see Fig. 3) consist of two doublet components with different contributions and quadrupole splitting. The hyperfine interactions parameters presented in Table 2 are indicative

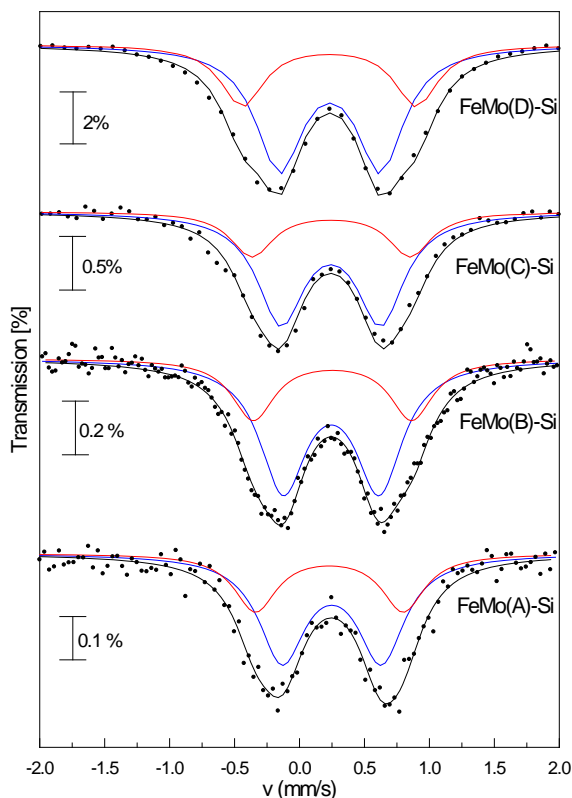


Fig. 3. ^{57}Fe Mössbauer spectra measured at RT for different metal content.

Table 2. The hyperfine interactions parameters fitted in the ^{57}Fe Mössbauer spectra of iron-molybdenum silica modified oxide systems. *B* – relative weight of the doublet components (Db2/Db1) in the spectra

Sample	IS1 (mm/s)	IS2 (mm/s)	QS1 (mm/s)	QS2 (mm/s)	<i>B</i>
Fe-Mo(A)-Si	0.32	0.34	1.14	0.76	0.50
Fe-Mo(B)-Si	0.34	0.33	1.22	0.74	0.57
Fe-Mo(C)-Si	0.33	0.33	1.22	0.76	0.63
Fe-Mo(D)-Si	0.32	0.32	1.34	0.77	0.54

of Fe^{3+} ions in high spin state in a surroundings of different symmetries. First doublet (QS1) with higher QS value corresponds to the tetrahedral oxygen surrounding and can be attributed to Fe^{3+} ions isomorphously incorporated into the silica framework. However, these atoms are not so strongly bounded with silica as in fayalite (Fe_2SiO_4) whose formation was observed in a high temperature reduction process of MCM-41 impregnated with Fe [11]. An observed increase of QS1 value from 1.14 mm/s for FeMo(A)-Si sample to 1.34 mm/s for FeMo(D)-Si one indicates an increase of a structural disorder in silica material. For higher Fe and Mo content, the larger structure deformation is expected. It is in agreement with the results of nitrogen adsorption/desorption isotherms measurements.

The second doublet is a result of free recoil absorption in ^{57}Fe probes highly dispersed in iron oxide nanoparticles in silica pores. The nature of this component can be revealed on the basis of Mössbauer measurement at LN_2 temperature. Mössbauer spectra for FeMo(D)-Si sample recorded at the RT and the LN_2 temperatures are shown in Fig. 4. The low temperature spectrum consists of two doublets and sextet with low intensity. The sextet appearance at low temperature testifies to the occurrence of iron oxides nanoparticles in superparamagnetic state.

The magnetic phase contribution in the investigated FeMo(D)-Si sample is equal approximately to 5%. Simultaneously, the presence of doublet and a low in-

tensity sextet component at LN_2 suggests that crystallite sizes are very small.

On the basis of intensities of doublet components derived from room-temperature Mössbauer spectra (see Table 2), it is clear that with the increasing metal content in the sample more and more iron oxide nanocrystallites are formed in silica pores.

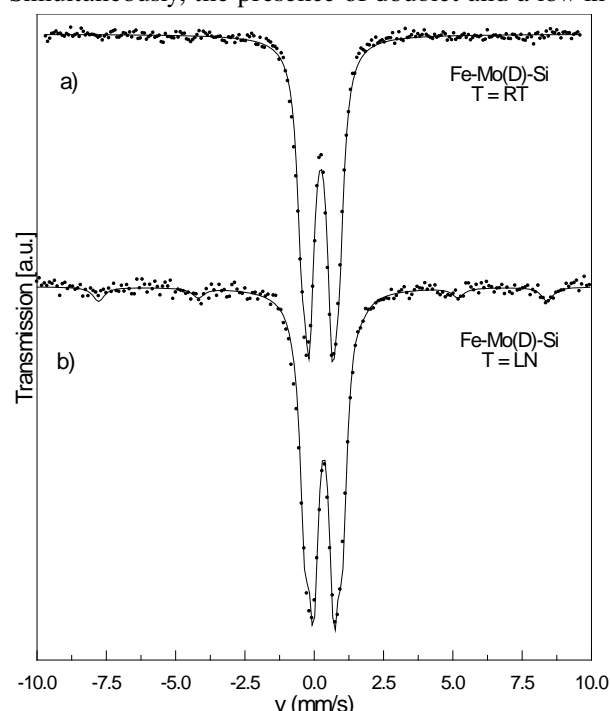
Conclusions

An introduction of different amounts of iron and molybdenum compounds to the synthesis mixture of the mesoporous silica led to the modification of the structural and surface properties of materials. The presence of surfactants and silicon compounds ensured formation of the small oxide species. It is also confirmed by the presence of the superparamagnetic phase revealed by Mössbauer spectroscopy. The amounts of oxide species in this state in the investigated samples are increased with increasing metal content.

In order to obtain the catalytic system with high activity, suitable selectivity and thermal stability, the optimum metal content should be determined. An excessive metal content induces structural changes of a MCM-41 support and leads to the formation of larger crystallites thus decreasing active surface of catalyst and changing redox properties.

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**Fig. 4.** ^{57}Fe Mössbauer spectra for Fe-Mo(D)-Si sample measured at RT (a) and (b) LN_2 (b).

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