Synthesis and characterization of iron-cobalt nanoparticles embedded in mesoporous silica MCM-4l

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Abstract. $Fe_{1-x}Co_x$/MCM-41 nanocomposite materials were prepared by wet impregnation of the silica mesoporous support with aqueous solution of iron and cobalt salt mixtures. Samples, after calcination, were reduced at 573 K in order to obtain homogeneous distribution of $(Fe\text{-}Co)_3O_4$ oxide species over the MCM-41 support. Bimetallic systems were achieved through high temperature reduction, carried out at 1073 K. The temperature-programmed reduction studies indicated complex nature of the oxide species. The phase analysis of the obtained samples after low temperature reduction process carried out by means of X-ray diffraction method and using ^{57}Fe Mössbauer spectroscopy revealed the presence of nanostructured magnetite- and maghemite-like phases. The samples with higher cobalt contents ($x \geq 0.2$) contained additionally bimetallic phases. The complete transformation of oxide phases to bimetallic Fe-Co systems occurred during reduction process in hydrogen at 1073 K. It was observed that high temperature processing caused partial transformation of highly dispersed iron oxide nanocrystallites into fayalite species embedded in the silica walls.

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

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Introduction

Nanosized materials reveal unique properties, which are intermediate between those characteristic at atomic level for molecules and those for bulk materials [14]. Such materials have found wide applications in the fields ranging from storage information technology [11] through catalysts in chemical technology [1] to biomedical applications [13]. Iron and cobalt catalysts have been extensively studied in the processes of CO and H_2 conversion to the liquid hydrocarbons via the Fischer-Tropsch (FT) synthesis [9]. Recently, one can observe the renewed interest in this process [2, 3, 6]. FT synthesis can be used for production of valuable chemicals and fuels not only from coal but also from renewable sources, such as biomass or wastes. Many studies have been devoted to the improvements of the properties of iron-cobalt catalysts by the development of new systems with suitable electronic interactions between metal species or by increasing the number of exposed active sites [8, 10, 11, 15]. The investigations were mainly focused on the effects of dispersion, reducibility, preparation conditions, calcination or reduction temperature.

Different porous media have been used for stabilization and modification of the properties of metallic

or metal oxide nanoparticles [4]. Iron-cobalt based nanocrystallites can be prepared by the impregnation of ordered silica mesoporous matrices, such as MCM-41 or MCM-48. The main advantage of such a method is that the supports allow formation of the small species within the uniform pores of well controllable size. High total surface area and large pore volume of these materials facilitate development of the catalysts with high active surface area.

The aim of the present paper was to determine the influence of composition and pretreatment conditions on the phase composition, redox and magnetic properties of the iron-cobalt catalysts supported on the MCM-41 silica mesoporous materials.

Experimental

The synthesis of MCM-41 silica support was accomplished using the procedure detailed described in [5]. In order to prepare 5 wt.% oxide iron-cobalt systems on the MCM-41 support, solutions of iron and cobalt nitrates were initially mixed in appropriate ratio and then used for the impregnation of the MCM-41 silica material. The samples were then subjected to low temperature treatment (drying) at 423 K for 1 h and next, were calcined in air atmosphere at 573 K for 1 h. As a result, the oxide systems of general formula $(Fe_{1-x}Co_x)O_y$/MCM-41 were formed. The samples in the next stage were reduced in hydrogen atmosphere at 573 K (low temperature reduction) for 4 h. The time of heating and cooling was 40 min. Samples were denoted as Fe-CoX/MCM-41, where X stands for the molar ratio of Fe/Co.

In order to prepare iron-cobalt bimetallic systems supported on the MCM-41 silica, the samples were reduced in the flow of hydrogen at high temperature and then were passivated. In order to realize this reduction a sample was placed in a quartz flow reactor. The flow rate of 6% H_2-Ar mixture was 30 cm^3/min. The temperature of reactor was maintained at 1073 K for 3 h. Then, the sample was cooled to room temperature, flushed with helium (0.5 h at a flow of 30 cm^3/min) and next passivated in the flow of 5% O_2-He mixture (0.5 hour at the flow of 30 cm^3/min). The procedure allowed the formation of a thin oxide layer on the surface of the metal crystallites and prevented deep oxidation of the species. The temperature-programmed reduction (TPR) studies of the samples after low-temperature reduction were carried out in an AMI-1 apparatus (Altamira Instruments Inc.).

The X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) measurements were performed for the samples after low and high temperature reduction treatment. XRD patterns were measured by means of a Philips X'Pert PW 3040/60 using diffractometer with CuK_α radiation at room temperature. They were fitted using the FULLPROF program for Rietveld refinement method.

The ^{57}Fe Mössbauer spectra were measured in transmission geometry at different temperatures using a constant acceleration spectrometer with a ^{57}Co/Rh source. The isomer shift, IS, was calibrated against a metallic iron foil at room temperature.

Results

Temperature-programmed reduction is a technique used for the characterization of solid materials in the field of heterogeneous catalysis. In this method, the sample of catalyst in the oxidized form is submitted to a programmed-temperature rise, while a reducing gas mixture is flowed over it. The rate of hydrogen consumption vs. temperature reflects the set of reactions occurred in the sample:

(1) $MeO_x + \delta H_2 \rightarrow MeO_{x-\delta} + \delta H_2O$
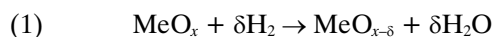
Thus the reduction temperature reveals the strength of metal-oxygen (MeO) bonds, and the intensity of signal is proportional to the amounts of suitable oxygen species. From the practical point of view, this method is also used to find best reduction conditions to achieve optimal properties of catalysts [7].

The TPR profiles of the samples are presented in Fig. 1. Studies indicate the complex interactions between iron and cobalt oxides, and with the support. The unambiguously assignment of TPR maxima to the reduction of specific oxide phases is very difficult. The reduction of the oxide phases in the studied iron-cobalt samples starts at low temperature, at about 470 K. A few maxima are observed for the sample without cobalt (the lowest curve) in temperatures ranging from 470 to 1100 K as results of successive reduction of different oxide phases. The maximum at about 620 K can be ascribed to the reduction of Fe_2O_3 species, accordingly to the reaction equation:

(2) $3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$
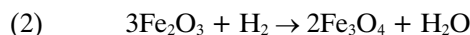
The peak at 940 K corresponds to the transformation:
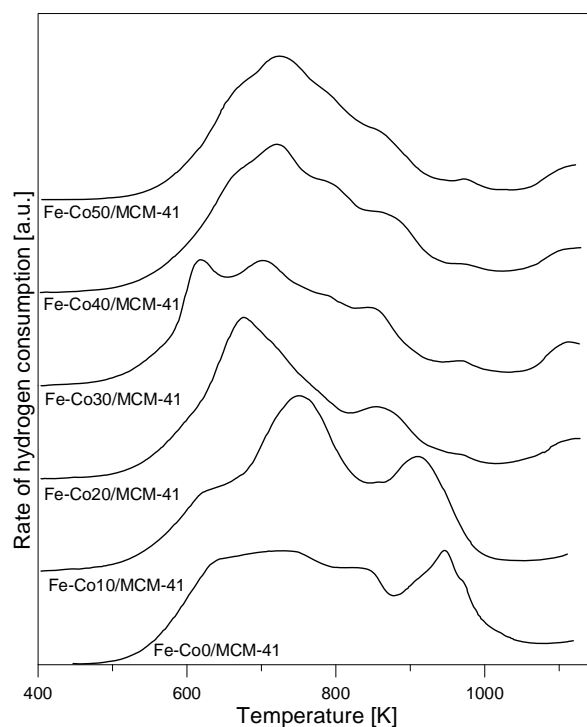
Fig. 1. TPR curves of iron-cobalt silica modified oxide systems.

(3) $Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$
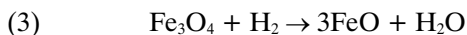
Complete reduction to the metallic Fe hardly occurred at the temperatures above 1050 K:

(4) $FeO + H_2 \rightarrow Fe + H_2O$

The additional overlapping peaks result from complex metal oxide-support interactions. Large oxide aggregates lying in inter-grain spaces are reduced more easily than oxide phases located in the support pores. The effects may also result from diffusion processes, for example, retardation of reduction due to the presence of water vapour in the nanochannels of silica support. Moreover, the interaction of silica with iron oxides leads to the formation of surface or bulk silicate compounds, such as fayalite, which are difficult to reduce (due to strong metal-oxygen interactions). Samples, prior to TPR measurements, were initially reduced at low temperatures, so partial transformation of iron oxides, especially large crystallites located on the peripherals of the silica grains, to the oxides with lower oxidation states and then re-oxidation after exposition to air could not be excluded.

An introduction of cobalt initiates a number of effects, which influence changes of metal-oxygen interactions. The maxima located at 740 K and 840 K move to lower values with an increase of Co content. The increased signal intensity in the range of lower temperatures is a consequence of the reduction enhancement. One can also observe a slight shift of difficult to reduce phases with maxima at 1100 K. The strongest effects of the facilitation of reduction are visible for the Fe-Co30/MCM-41 sample.

The observed effects may result from several reasons. The reduction of cobalt oxides is a multi-stage process, and maxima in the TPR corresponding to them could overlap peaks from iron oxides.

Large aggregates of Co_3O_4 are reduced in the similar range of temperatures as Fe_2O_3. However, highly dispersed oxide species, which often form surface or bulk chemical compounds with silica can be reduced at very high temperatures.

Intimate contact of iron and cobalt oxide phases facilitates mutual interactions. Thus partial reduction of one of the system components may improve hydrogen activation and further transfer to the second component of oxide system. Moreover, the presence of cobalt can cause point or macroscopic crystallographic lattice distortions in iron oxides, which may facilitate reduction. On the other hand, high temperature treatment favors the formation of chemical compounds between iron and cobalt oxides in different oxidation states, e.g. with the spinel structures. The reduction of the oxide species located in the silica channels or strongly dispersed on the silica grains give a chance to the formation of alloy and bimetallic compound between iron and cobalt.

XRD patterns for selected samples after low (573 K) and high (1073 K) temperature reduction treatment are shown in Fig. 2. The broadened halo at 2θ angles between 20 and 30° results from the amorphous silica support. Refinement by the Rietveld method of well-resolved peaks in the pattern for the sample Fe-Co10/MCM-41 revealed the presence of maghemite- and/or magnetite-like oxide phases with a partial replacement of some Fe atoms with Co ones. The lattice parameter is equal to 8.37(1) Å. The second bimetallic phase appears with increasing cobalt content, which is well visible in the pattern for the sample Fe-Co40/MCM-41 (Fig. 2a, upper pattern). The Bragg peaks related to the bimetallic phase are denoted by triangles. The bimetallic contribution achieves a maximum value for the Fe-Co30/MCM-41 sample.

The reduction at 573 K caused the transformation from hematite to maghemite or magnetite with spinel-like structures and, as a consequence a mixture of Fe_2O_3 and Fe_3O_4 is not observed. However, in the samples with $x < 0.1$ reduction process performed at low temperature was sufficient in order to partially reduce the oxide phase to a bimetallic form.

In the samples after high temperature reduction (Fig. 2b) two phases were identified in the whole range of Co content. The first is bimetallic $Fe_{1-x}Co_x$ and the second is $(Fe_{1-x}Co_x)_2SiO_4$ compound. The contribution of bimetallic phase was changed with Co content
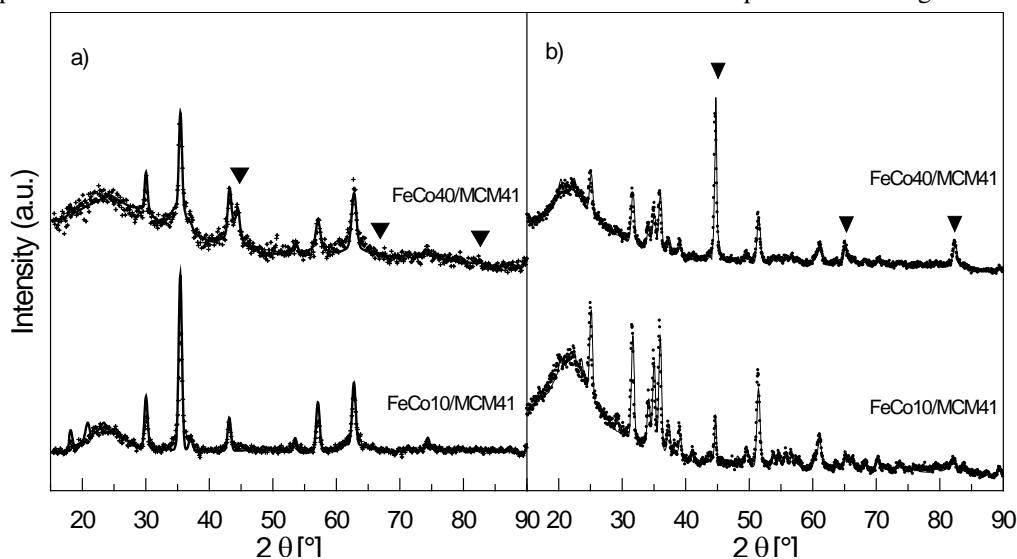

Fig. 2. XRD patterns of selected samples after low temperature (573 K) reduction (a) and high temperature (1073 K) reduction (b). The full curves represent calculated patterns, the points – the observed ones. Full triangles up the diffraction pattern indicate the bimetallic Fe-Co phase.

from 0.05(3)% to 0.40(5)% for Fe-Co0/MCM-41 and Fe-Co30/MCM-41 sample, respectively. Formation of silicate compounds may result from the direct reaction of partially reduced oxides with silica at high temperatures during thermal treatment.

Figure 3 shows the Mössbauer spectra of the series of $(Fe_{1-x}Co_x)$/MCM-41 samples after low temperature reduction process measured at room temperature. All spectra consist of sextets with low intensity and one doublet. Two sextets are related to Fe atoms located at two non-equivalent tetrahedral (A) and octahedral (B) sites in the magnetite-like structure. In pure magnetite the relation of occupancies of A and B sites is equals to 1:2. In the obtained spectra this relation is clearly distorted. This experimental result points to the necessity of taking into account one more sextet component in the fitting procedure. All the values of hyperfine interactions parameters for the third component are close to the values for Fe probes in maghemite. For the samples with $x \geq 0.2$, the fourth sextet appeared. This component is related to bimetallic Fe-Co phase. A central doublet with an isomer shift of about 0.33(2) mm/s and QS of 0.86(5) mm/s indicate the presence of iron in a paramagnetic state.

From Mössbauer measurements at different temperatures for the sample Fe-Co30/MCM-41 after low temperature reduction, it is evident that the relative contribution of the paramagnetic component increases from 8(3)% at 14 K to 49(4)% at 600 K in relation to
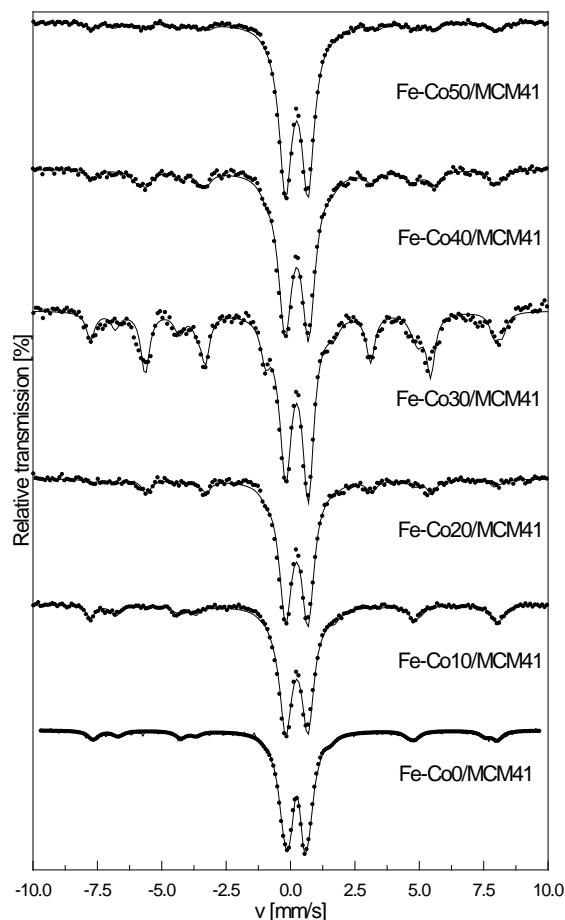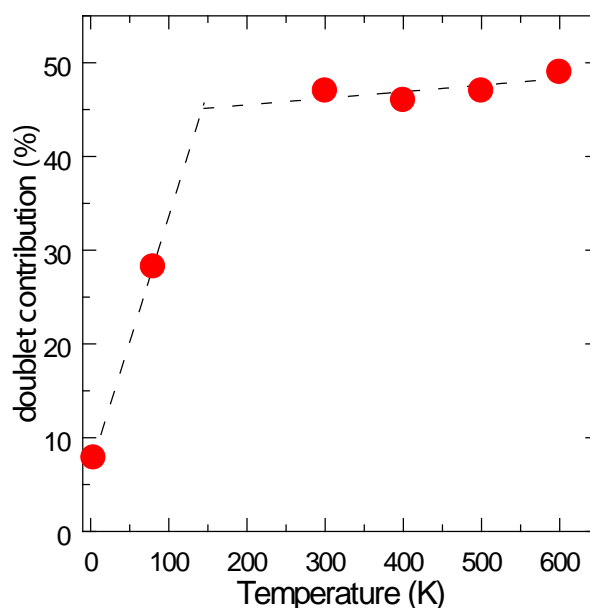

Fig. 4. The superparamagnetic phase concentration as a function of temperature for the sample Fe-Co30/MCM-41 measured after low temperature reduction process.

the total MS signal (Fig. 4). The paramagnetic component represent the superparamagnetic phase (SPM) resulting from the relaxation phenomenon due to the intrinsic finite-size effect. The temperature dependence of SPM phase contents presented in Fig. 4 has nonlinear character. In the range of temperatures from 14 K to about RT this content increases rapidly but above RT its contribution remains almost constant. This dependence results from the occurrence of two different crystallites groups with different mean sizes located in the silica support. The smaller crystallite demonstrating superparamagnetic behavior are located in pores, the bigger ones exhibit ferromagnetic ordering in inter-grain spaces [12]. The contributions of all phases occurring in the investigated samples are presented in Fig. 5.

Room-temperature Mössbauer spectra of the samples after high temperature reduction are presented in Fig. 6. The obtained spectra consist of one sextet and two doublets. The sextet has hyperfine interactions parameters similar to the analogous parameters of metallic iron. The isomer shift values for all the samples were equal to 0.00(2) mm/s and QS about –0.02(1) mm/s. The induction of hyperfine magnetic field for the sample without Co was 33.3(1) T and this value increases monotonically to 36.1(1) T for the sample Fe-Co50/MCM-41.

The doublets are assigned to Fe^{2+} and Fe^{3+} ions in the octahedral M1 or M2 sites of $(Fe-Co)_2SiO_4$ modified fayalite phase.

In the result of high temperature reduction process the highly dispersed in MCM-41 matrix Fe/Co oxide nanoparticles (SPM phase before this process) interact with the walls of silica nanochannels to form fayalite. In a consequence, the doublet related to SPM phase disappears completely in the MS spectra after reduction. The Fe/Co oxide nanocrystallites of the larger sizes are reduced to bimetallic Fe/Co nanoparticles. In this way ferromagnetic Fe nanoparticles stabilized with Co addition were obtained in the nanocomposite. The bimetallic Fe-Co phase contribution as a function of
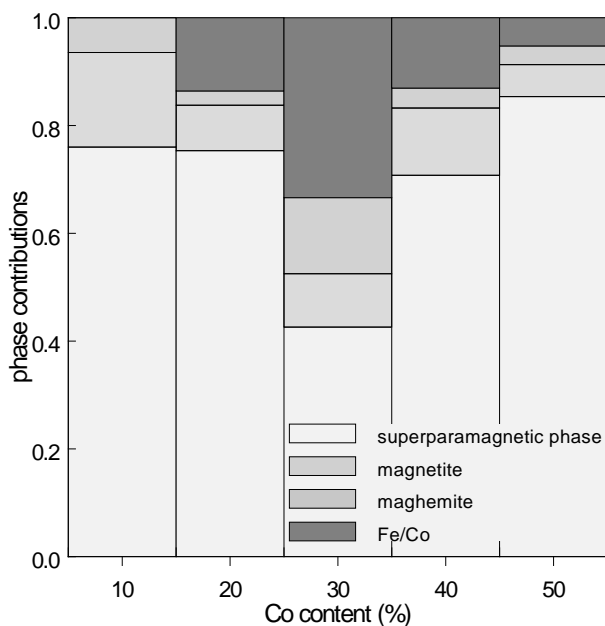

Fig. 3. Room-temperature Mössbauer spectra for the samples after low temperature reduction as a function of Co content.

Fig. 5. The phase contributions vs. the Co content for the samples after low temperature reduction derived from room--temperature MS spectra.

Co content is shown in Fig. 7. The maximum bimetallic phase contribution occurs for the samples with a cobalt content of $x = 0.3$.
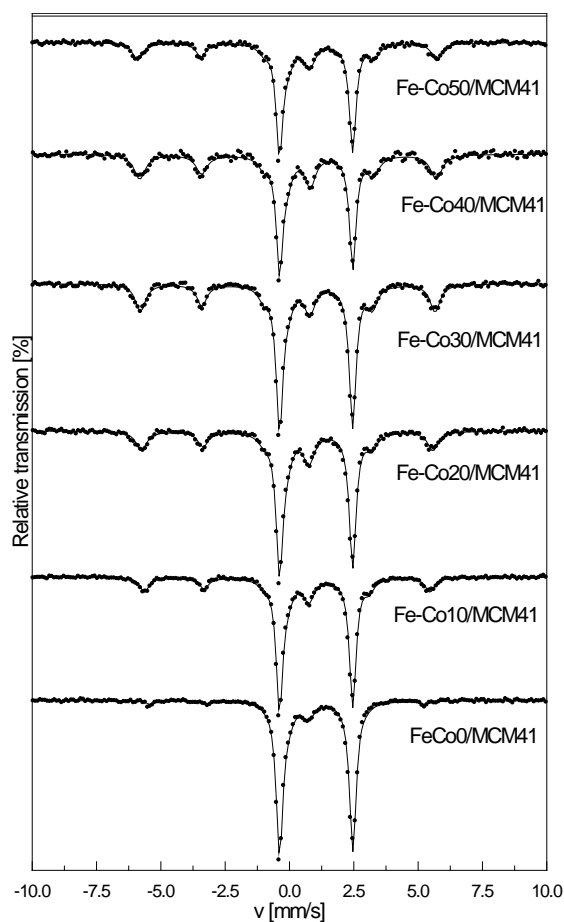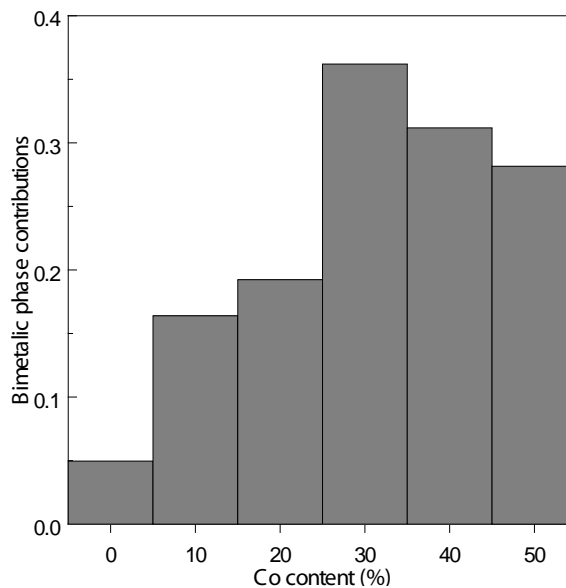

Fig. 7. The bimetallic Fe-Co phase contributions vs. Co content for the samples after high temperature reduction derived from room-temperature MS spectra.

Conclusions

Ordered mesoporous materials of MCM-41 type can be used as a support for magnetic nanoparticles. Nanocrystallites of iron oxides located in silica pores exhibit a superparamagnetic behavior. The nanoparticles with sizes of the order of 40 nm mainly located in the inter-grain spaces create a stable metallic phase which is not oxidized in the atmosphere. The high temperature reduction leads to chemical transformation of a part of the highly dispersed oxides phases to the fayalite. The optimal Co content to obtain maximum bimetallic phase contributions was determined as being equal to 30 wt.%.

Fig. 6. Room-temperature Mössbauer spectra for the samples after high temperature reduction as a function of Co content.

References

1. Ambashta RD, Yusuf SM, Mukadam MD, Singh S, Wattal PK, Bahadur D (2005) Physical and chemical properties of nanoscale magnetite-based solvent extractant. J Magn Magn Mater 293:8–14
2. Balat M, Balat M, Kırtay E, Balat Ha (2009) Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 2: Gasification systems. Energy Convers Manage 50:3158–3168
3. Demirbas A (2008) Hydrogen production from carbonaceous solid wastes by steam reforming. Energy Sources Part A 30:924–931
4. Gac W, Goworek J, Wójcik G, Kępinski L (2008) The properties of gold catalysts precursors adsorbed on the MCM-41 materials modified with Mn and Fe oxides. Adsorption 14:247–256
5. Grün M, Unger KK, Matsumoto A, Tsutsumi K (1997) Ordered microporous/mesoporous MCM-41 type absorbents: novel routes in synthesis, product, characterisation and specification. In: McEnaney B, Mays JT, Rouquerol J, Rodriguez-Reynoso J, Sing KSW, Unger KK (eds) Characterization of porous solids IV. The Royal Society of Chemistry, London, pp 81–89
6. James OO, Chowdhury B, Mesubic MA, Maity S (2012) Reflections on the chemistry of the Fischer-Tropsch synthesis. RSC Adv 10:1–20

7. Khan A, Smirniotis PG (2008) Relationship between temperature-programmed reduction profile and activity of modified ferrite-based catalysts for WGS reaction. J Mol Catal A: Chem 280:43–51

8. Li B, Xu J, Li X, Liu J, Zuo S, Pan Z, Wuc Z (2012) Bimetallic iron and cobalt incorporated MFI/MCM-41 composite and its catalytic properties. Mater Res Bull 47:1142–1148

9. Ma X, Sun Q, Ying W, Fang D (2009) Effects of the ratio of Fe to Co over Fe-Co/SiO2 bimetallic catalysts on their catalytic performance for Fischer-Tropsch synthesis. J Nat Gas Chem 18:232–236

10. Manova E, Paneva D, Kuneva B *et al.* (2009) Mechanochemical synthesis and characterization of nanodimensional iron-cobalt spinel oxides. J Alloys Compd 485:356–36

11. Moser A, Takano K, Margulies DT *et al.* (2002) Magnetic recording: advancing into the future. J Phys D 35:R157– R167

12. Surowiec Z, Wiertel M, Zaleski R, Budzyński M, Goworek J (2010) Positron annihilation study of iron oxide nanoparticles in mesoporous silica MCM-41 template. Nukleonika 55;1:91–96

13. Thünemann AF, Schütt D, Kaufner L, Pison U, Möhwald H (2006) Maghemite nanoparticles protectively coated with poly(ethylene imine) and poly(ethylene oxide)-block-poly(glutamic acid). Langmuir 22:2351–2357

14. Tronc E, Jolivet JP (1992) Interaction between charged particles. In: Dormann JL, Fiorani D (eds) Magnetic properties of fine particles. North-Holland Publishing, Amsterdam, pp 199–204

15. Tsoncheva T, Ivanova L, Paneva D, Mitov I, Minchev C, Fröba M (2009) Cobalt and iron oxide modified mesoporous zirconia: Preparation, characterization and catalytic behaviour in methanol conversion. Microporous Mesoporous Mater 120:389–396