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Investigation of biogenic iron-containing nanoscale composite materials

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Abstract Biogenic composites are interesting as green and sustainable precursors for preparation of advanced materials of various applications. Biomaterials from *Leptothrix* group bacteria cultivated in two feeding media of silicon-iron-glucose-peptone (SIGP) and Lieske were studied. Iron-containing biogenic powders and biofilms on silica gel covered aluminum plates were prepared. They were studied to elucidate the effect of the plates in the process of growing biogenic iron nanotubes. The cultivation period was varied from 4 to 30 days. Biomass phase composition and physicochemical properties were studied by Mössbauer spectroscopy at room and low temperature, as well as by means of powder XRD, FTIRS, and SEM methods. Mössbauer analysis offered us a unique possibility to register iron oxide species at the different steps of biogenic material formation. Tetrahedrally coordinated iron species were registered at an early stage of biofilm formation. So, important results on the mechanism of biomineralization process are obtained. The reaction of CO oxidation on prepared biomaterials was studied using in situ DRIFTS. Comparative analysis of the obtained materials and examination of spent samples showed differences in their phase composition, stability and dispersity. Changes of the phase composition were observed during catalytic tests with biomasses obtained in Lieske feeding media. No differences in biogenic powder and biofilm composition and dispersity were registered when

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SIGP media was used neither for studied bacteria cultivation period nor in spent catalysts. These results indicated the stabilizing effect of extra silicon content in the feeding media. Formation of iron oxihydroxide nanotubes was also established in this case.

Keywords Biogenic nanosized iron oxides · *Leptothrix* genus of bacteria · Mössbauer spectroscopy · X-ray diffraction · IR spectroscopy

1 Introduction

Recently, modern science and technologies have faced a number of big challenges due to limited energy and raw materials resources and their unsafe use. Unusual characteristics of biogenic materials have attracted a great interdisciplinary interest and inspired numerous ideas for their applications in order to expand energy and raw material sources, to reduce the release of harmful substances, to solve environmental problems, to improve the quality of life and to treat various diseases [1–5]. The biogenic iron-containing materials are products of iron-transforming bacteria lifecycle [4, 5]. They are widely spread in nature. *Leptothrix* genus species are typical inhabitants of ferrous-containing waters that oxidize iron ions by forming significant amounts of insoluble oxihydroxides in their sheaths [4–8]. These hydroxide materials have variable phase composition, different shape (globules, tubes, etc.) and sizes as well as varying degree of self-organization, consolidation, chemical reactivity, and stability. The properties of the biogenic materials can additionally be regulated by altering the composition of the cultivation media or by biogenic material deposition on different substrates [2, 3, 7–12]. In this regard, cultivation of iron bacteria under different laboratory conditions gives new technological solutions and reveals opportunities for preparation of a large number of useful materials on "green" and sustainable way. A major advantage of bio-production is the complete removal or limitation of solvents and expensive and harmful chemicals use. The obtained biogenic materials show unique properties. They often contain nanosized particles, and demonstrate high specific surface area and high reactivity, which give a prospect of high degree of adsorption and decomposition of various pollutants [9–16]. Currently, considerable attention has been given to studies of nanodimensional iron-containing materials as an advanced area of biogenic material science with high application potential in nanotechnology, green and eco-technologies, novel materials, information technologies, etc. However, laboratory synthesis of such a specific structure and especially preparation of iron oxihydroxide nanotubes is a big challenge [3, 4]. Some well-known chemical relations are still not set here. Prepared biogenic nanoparticles exhibit low thermal and long-term stability, which is still an open question. On the other hand, different inorganic elements such as silicon have an impact on the formation of highly dispersed iron particles [17]. Si incorporation into the biogenic microstructures is expected to provide an attractive approach to study industrial application of bacteria-produced iron oxides. Special attention has been paid to silicon impact on inhibition of Fe mineral crystallization and Si promotion effect on anisotropic crystal growth [9–12]. An improvement in biotechnology procedure of iron oxide/hydroxide biogenic material preparation using the *Leptothrix* bacteria strain is based on an optimization of inoculation conditions, change of nutrient composition and/or deposition of biogenic material on different substrates [1–4].

The aim of the present paper was to investigate the stabilization effect of silicon in the cultivation media and silica gel plate coverage on the growing process of biogenic iron-containing nanotubes in laboratory conditions. Based on our previous results [10, 16] two very effective feeding media of silicon-iron-glucose-peptone (SIGP) and Lieske were used

Table 1 Composition and pH of used feeding media

Cultivation medium	Start pH	Final pH	Medium composition
Lieske	7.22	7.71	$Mg(HCO_3)_2$ saturated solution 1:10, K_2HPO_4 traces, $MgSO_4.7H_2O$ traces, distilled water, iron grits, $FeSO_4$
Silicon-iron-glucose-peptone (SIGP)	7.03	7.41	Glucose, Bacto peptone, $MgSO_4.7H_2O$, $K_2HPO_4.2H_2O$, $Na_2HPO_4.12H_2O$, $Na_2SiO_3.9H_2O$, $CaCl_2$, $FeSO_4$, HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesulphonic acid)

to study the mechanism of biomineralization process. The catalytic behavior of selected samples was also tested in the reaction of CO oxidation.

2 Experimental

2.1 Materials

Series of powder and supported iron-based biogenic materials were obtained by cultivation of laboratory isolated *Leptothrix* genus of bacteria in nutrition media of silicon-iron-glucose-peptone (SIGP) and Lieske [6, 18]. Their composition is presented in Table 1. Biogenic iron-containing biofilms were prepared using silica gel covered plates (0.2 mm Silikagel SiO_2 film on Al plate, DC-Alufolien, Merck). Unsupported powder materials were collected from the same media for comparison. In case of Lieske medium, the cultivation was done by using Ferenbach flasks under static conditions at room temperature. For the SIGP medium, the flasks were mounted on a shaker machine and swirled at 70 rpm. The cultivation period was between 4 and 30 days in order to collect data on biomineralization process dynamics. The obtained powder biomass was separated by decantation and filtration of the solution. It was washed several times with distilled water and dried at 40 °C.

2.2 Characterization methods

Powder X-ray diffraction patterns were collected within the range of 5.3 to 80° 2θ with a constant step 0.02° 2θ on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. Phase identification was performed with the Diffrac*plus* EVA using ICDD-PDF2 Database. Topas-4.2 software package was used to determine the mean crystallite size using the fundamental parameters and peak shape description including appropriate corrections for the instrumental broadening and diffractometer geometry.

Mössbauer spectra were recorded by Wissenschaftliche Elektronik GmbH electromechanical apparatus (Germany), operating at a constant acceleration mode. An α-Fe standard and a ^{57}Co/Rh source were used. The Mössbauer spectra were collected at room temperature and at the liquid nitrogen temperature. The parameters of hyperfine interactions of the obtained spectral components: isomer shift (IS), quadrupole splitting (QS), hyperfine effective field (H_{eff}) as well as line width FWHM and component relative weight (G) were determined by CONFIT program. Computer fitting was based on the least squares method.

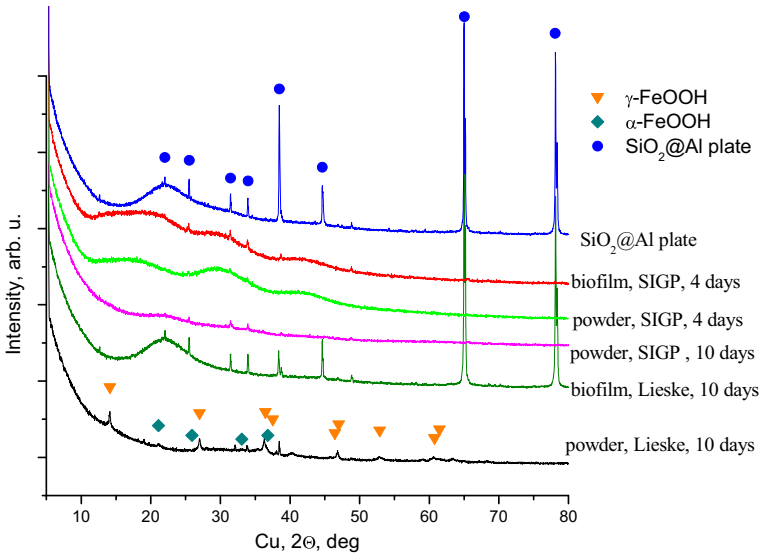


Fig. 1 X-ray diffraction patterns of powder and SiO_2@Al plate deposited iron-based biogenic materials obtained in SIGP and Lieske nutrition media. The diffraction pattern of the support is also presented for comparison

FTIR spectra of the materials in KBr pellets were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) in the middle-IR region. In addition, some materials were studied in a model catalytic reaction of CO oxidation by oxygen using a high-temperature/vacuum chamber accessory (Thermo Spectra-Tech, USA) working in diffuse-reflectance mode (DRIFTS). Spectra were collected in the range 1111–4000 cm^{-1} determined by the transparency of CaF_2 windows that were used in the measuring cell. The catalytic measurements were carried out using a flow mixture (88 ml/min) of $Ar:O_2:CO = 80:11:9$ (as vol.%) at reaction temperatures up to 250 °C. The temperature was raised by a heating rate of 10 deg/min followed by a 30-min soak at the respective level. Time interval of 30 minutes was accepted sufficient to obtain constant working conditions: stabilization of the material and of the gas phase composition in the measuring cell.

The morphology of the obtained biogenic materials was studied using a JEOL SEM T-200 scanning electron microscope. Before SEM observations, the samples were covered with vacuum-deposited carbon and gold films in order to amplify picture contrast.

3 Results and discussion

X-ray diffraction patterns of used SiO_2@Al plate as well as selected powder and supported iron-based biogenic materials obtained by cultivation of bacteria in SIGP and Lieske nutrition media are shown on Fig. 1. Sharp and intensive diffraction lines of used support are very well seen and marked on the figure. The biomaterial patterns demonstrate the presence of X-ray amorphous halo-peaks supported on the significant initial silica halo-peaks. Low intensity patterns of crystalline phases can be mentioned only in Lieske powder samples obtained after 10 days bacteria cultivation. The pattern positions match with the characteristic ones for an iron oxyhydroxide phases - lepidocrocite γ-FeOOH (PDF 44-1415)

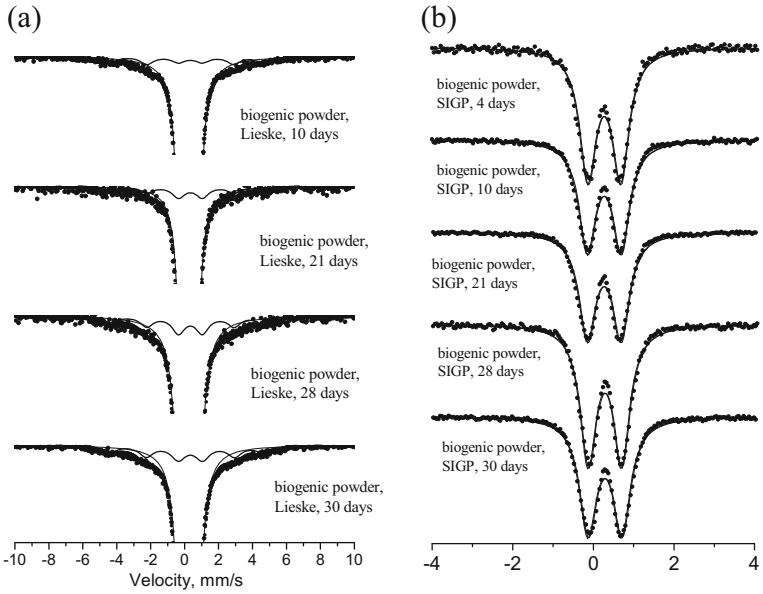


Fig. 2 Room temperature Mössbauer spectra of biogenic powder samples after mathematical fitting: **a** Lieske and **b** SIGP feeding media

and goethite α-FeOOH (PDF 81-0463) polymorphs. No characteristic patterns of any iron-containing phase were obtained in the SIGP diffractograms during the studied time interval (4–30 days).

Mössbauer spectroscopy was used to clarify details on presented iron-containing phases including X-ray amorphous ones. Figures 2 and 3 show room temperature (RT) Mössbauer spectra of biogenic powder samples and biofilms supported on SiO_2@Al plates after mathematical fitting. Paramagnetic doublet component(s) can be seen in all registered Mössbauer spectra but different quantity of non-resolved magnetically split sextet pattern is also presented in the Lieske samples. The calculated Mössbauer parameters of spectra components are given in Table 2. The best spectra fit of the paramagnetic part of RT spectra was done by using one or two summarized quadrupole components indicating that the oxidation state of the iron ions was Fe(III) in all samples (Table 2) [17]. Estimated isomer shift values of the doublet components (0.33–0.36 mm/s) and quadrupole splitting QS = 0.67–0.84 mm/s show the presence of octahedrally coordinated iron ions. These components could be attributed to the presence of various paramagnetic iron compounds having very close spectra at RT (probably γ-FeOOH or ferrihydrite) as well as to a superparamagnetic relaxation (SPM) of nanosized iron particles. Partial or complete separation of SPM phases and paramagnetic components will be set by low temperature Mössbauer spectra. Tetrahedrally coordinated Fe(III) ions were registered in biofilms prepared on a SiO_2@Al plate. At the early stages of biofilm formation the quantity of tetrahedrally coordinated Fe(III) ions was higher. In the case of Lieske nutrient media all iron ions were in tetrahedral positions. The amount of Fe(III)-tetrahedral ions decreased upon increasing the cultivation time. The observation of tetrahedrally coordinated Fe(III) ions could be assigned to formation of iron species on the SiO_2@Al plate. Probably, this type of ions also exists at later stages of cultivation, but their quantity becomes very small with biofilm growing in comparison to the whole of

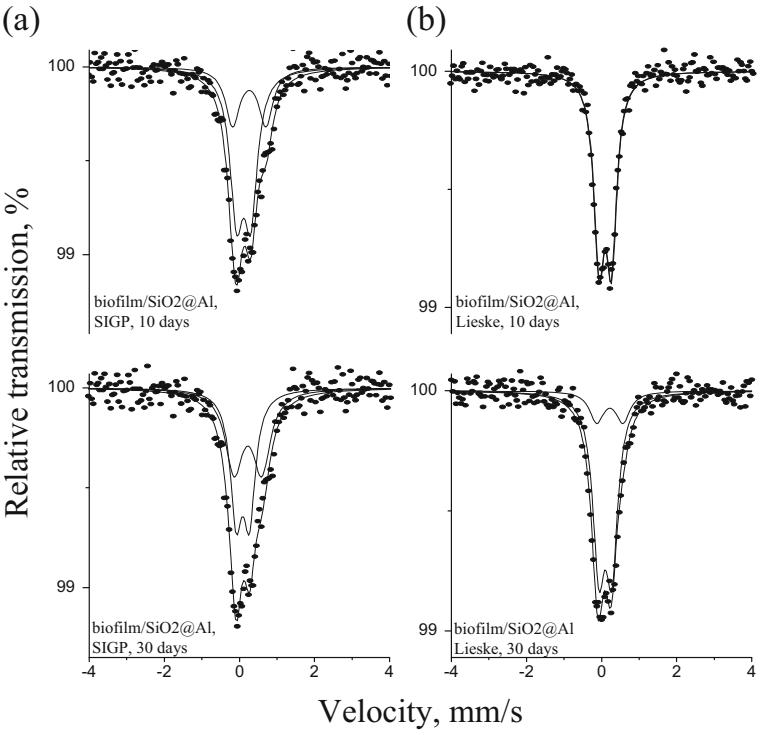


Fig. 3 Room temperature Mössbauer spectra of biofilms supported on the SiO_2@Al plates after mathematical fitting: (**a**) SIGP and (**b**) Lieske feeding media

iron-containing phases. A sextet component (Sx) is presented only in the samples obtained in Lieske feeding media. It has the characteristic hyperfine parameters of α-FeOOH [17].

Mössbauer spectra of selected samples were registered at the temperature of liquid nitrogen (LNT) in order to resolve presented SPM phases (Fig. 4). However, SIGP samples preserved the doublet type spectrum. In Lieske samples the main part of RT spectrum was resolved showing the characteristic hyperfine parameters of α-FeOOH particles. Calculated Mössbauer parameters are given in Table 2. Their hyperfine field values (H_{eff}) are relatively lower than the characteristic ones of bulk crystal phases, i.e. nanosize goethite particles of different sizes are registered [19, 20]. The obtained Mössbauer results are in very good agreement with powder XRD analysis showing nanometric size of registered iron oxyhydroxide crystallites (α-FeOOH and γ-FeOOH).

SEM images of selected samples are shown on Fig. 5. Formation of highly dispersed iron species is very well seen in all studied materials. Comparison reveals that smaller particles are prepared in SIGP feeding media which is in very good agreement with the other analyzes in present study. Figure 5 demonstrates differences in the material morphology of those samples. Preparation of iron oxihydroxide nanosized tubes in biogenic film SiO_2@Al plate in SIGP feeding media is very well seen (Fig. 5c, e) when nanotubes were singled out. Nanosized tubes in biogenic film SiO_2@Al plate in Lieske media were not registered even at higher magnification (Fig. 5d, f).

Additional information about chemical composition, chemical linkages and surface functional groups of the studied biogenic materials was obtained by IR spectroscopy (IRS) study.

Table 2 Mössbauer hyperfine parameters of spectra components of the studied samples measured at room temperature (RT) and at liquid nitrogen temperature (LNT)

Sample	Components	IS, mm/s	QS, mm/s	Heff, T	FWHM, mm/s	G, %
biofilm/SiO_2@Al, Lieske, 10 days	Db – Fe^{3+}_{tetra}	0.21	0.33	–	0.33	100
biogenic powder, Lieske, 10 days	Sx – α-FeOOH	0.32	−0.12	27.5	0.90	7
	Db – Fe^{3+}_{octa}	0.35	0.68	–	0.48	93
biogenic powder, Lieske, 21 days	Sx – α-FeOOH	0.32	−0.12	27.7	0.90	10
	Db – Fe^{3+}_{octa}	0.35	0.67	–	0.48	90
biogenic powder, Lieske, 28 days	Sx – α-FeOOH	0.32	−0.12	27.8	0.90	12
	Db – Fe^{3+}_{octa}	0.35	0.70	–	0.52	88
biofilm/SiO_2@Al Lieske, 30 days	Db1 – Fe^{3+}_{octa} Db2 – Fe^{3+}_{tetra}	0.33	0.70	–	0.45	18
		0.20	0.35	–	0.38	82
biogenic powder, Lieske, 30 days	Sx – α-FeOOH	0.32	−0.12	27.9	1.00	13
	Db – Fe^{3+}_{octa}	0.35	0.69	–	0.49	87
biogenic material Lieske, 30 days, after catalytic test	Sx1 – α-Fe_2O_3	0.34	−0.11	49.1	0.65	10
	Sx2 – γ-Fe_2O_3	0.32	0.00	33.7	2.00	27
	Db – Fe^{3+}_{octa}	0.33	0.81	–	0.60	63
biogenic powder, Lieske, 30 days, LNT	Sx1 – α-FeOOH	0.45	−0.11	45.3	1.09	36
	Sx2 – α-FeOOH,	0.45	−0.11	38.1	1.29	34
	CME Db – Fe^{3+}_{octa}	0.44	0.65	–	0.45	30
biogenic material, Lieske, 30 days, LNT after catalytic test	Sx1 – α-Fe_2O_3	0.45	−0.11	50.1	0.63	10
	Sx2 – γ-Fe_2O_3	0.43	0.02	44.5	1.49	83
	Db – Fe^{3+}_{octa}	0.43	0.83	–	0.50	7
biofilm/SiO_2@Al SIGP, 10 days	Db1 – Fe^{3+}_{tetra}	0.21	0.37	–	0.42	69
	Db2 – Fe^{3+}_{octa}	0.34	0.88	–	0.46	31
biogenic powder, SIGP, 4 days	Db – Fe^{3+}_{octa}	0.36	0.81	–	0.50	100
biogenic powder, SIGP, 10 days	Db – Fe^{3+}_{octa}	0.36	0.84	–	0.50	100
biogenic powder, SIGP, 21 days	Db – Fe^{3+}_{octa}	0.35	0.83	–	0.50	100
biogenic powder, SIGP, 28 days	Db – Fe^{3+}_{octa}	0.35	0.83	–	0.49	100
biofilm/SiO_2@Al SIGP, 30 days	Db1 – Fe^{3+}_{octa}	0.33	0.74	–	0.56	49
	Db2 – Fe^{3+}_{tetra}	0.19	0.35	–	0.38	51
biogenic powder, SIGP, 30 days	Db – Fe^{3+}_{octa}	0.35	0.84	–	0.52	100

Table 2 (continued)

Sample	Components	IS, mm/s	QS, mm/s	Heff, T	FWHM, mm/s	G, %
biogenic material after catalytic test, SIGP, 30 days	Db – Fe^{3+}_{octa}	0.34	0.97	–	0.60	100
biogenic powder, SIGP, 30 days, LNT	Db – Fe^{3+}_{octa}	0.44	0.87	–	0.56	100
biogenic material after catalytic test, SIGP, 30 days, LNT	Db – Fe^{3+}_{octa}	0.44	0.94	–	0.60	100

Db - quadrupole doublet; Sx - sextet component; CME – collective magnetic excitation behavior.

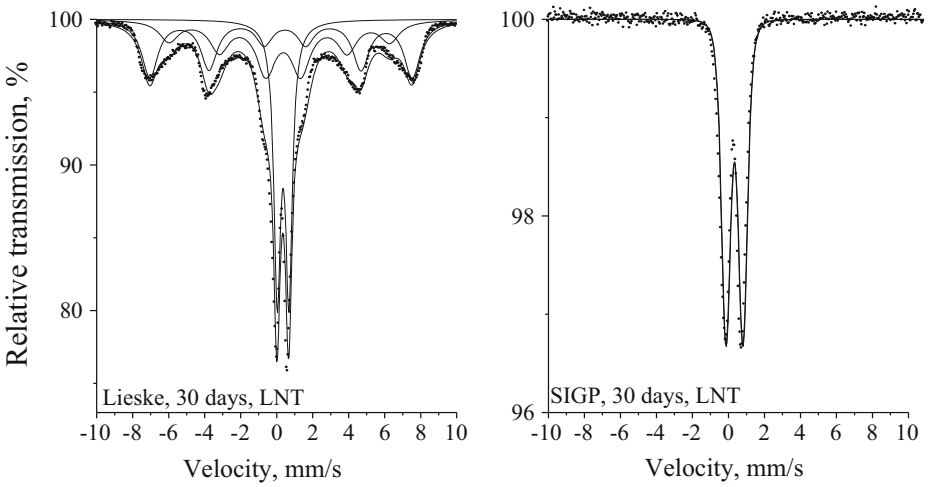
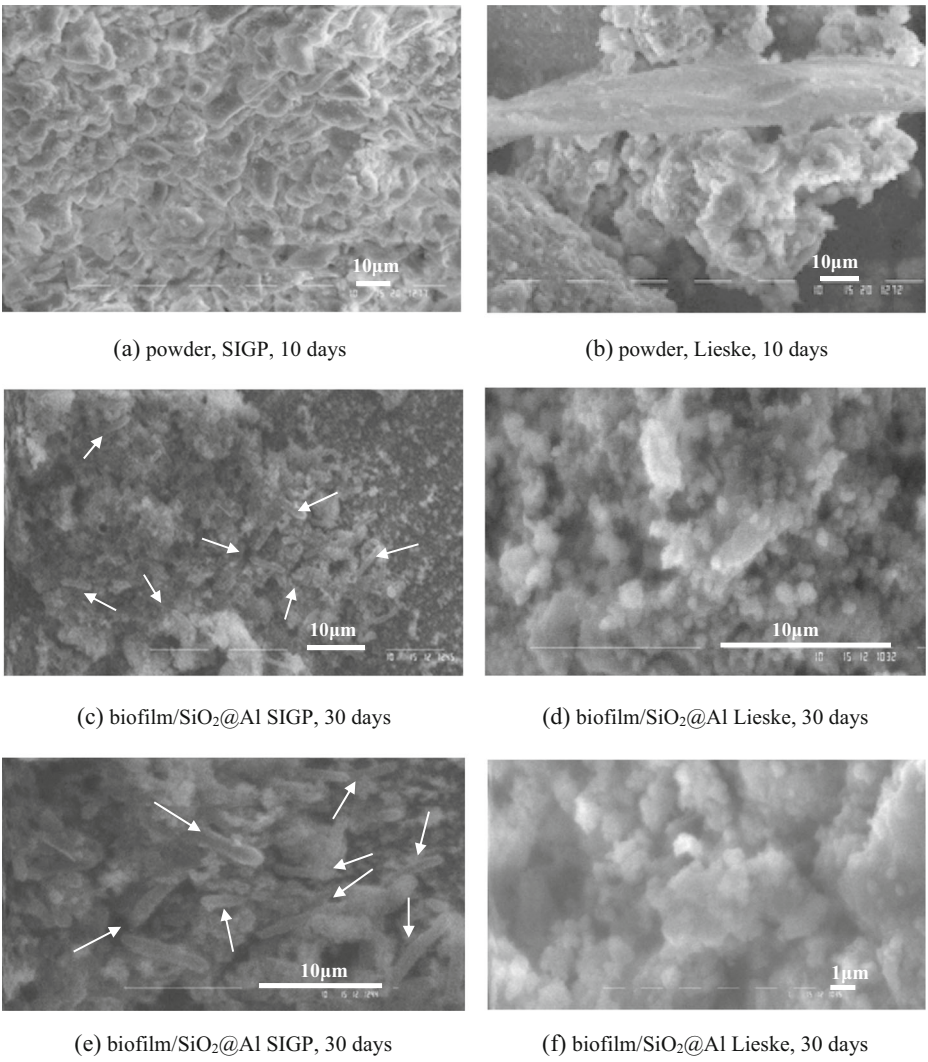


Fig. 4 Mössbauer spectra of biogenic materials measured at the temperature of liquid nitrogen

Spectra are shown on Fig. 6. Only bands characteristic of silicagel are observed in the spectrum of fresh SIGP powder sample. Collected spectrum is not informative about presence of biogenic iron because its characteristic bands are overlapped by the bands with strong intensity of the used support (Fig. 6a). Characteristic bands of γ-FeOOH (473, 748, 800, 925, 1024, 1140 and around 3180 cm^{-1}) are registered in the spectrum of biomass sample obtained in Lieske medium (Fig. 6b) [20–24]. The spectrum of Lieske sample demonstrates also bands originating from the cultivation medium residues as groups of CO_3 (1556, 1642, and 1662 cm^{-1}), PO_4 (wide band positioned around 1000 cm^{-1}) and SO_4 (450, 665, and 1128 cm^{-1}) [24, 25]. The Lieske medium has entirely inorganic character and the low intensity bands at about 2900 and 1271 cm^{-1} confirm that the final material contains rests of bacterial origin: fatty acid components from the cell membrane and polysaccharides from the bacterial capsule [26].



(a) powder, SIGP, 10 days

(b) powder, Lieske, 10 days

(c) biofilm/SiO_2@Al SIGP, 30 days

(d) biofilm/SiO_2@Al Lieske, 30 days

(e) biofilm/SiO_2@Al SIGP, 30 days

(f) biofilm/SiO_2@Al Lieske, 30 days

Fig. 5 SEM images of powder biomaterials and biofilms supported on the SiO_2@Al

Biomaterials' potential for application in catalysis was examined in the reaction of CO oxidation. The chemical reaction was studied in situ by diffuse-reflectance IRS (DRIFTS) (Fig. 7a, b). The decrease in integrated intensity of the CO gas phase band was used as a measure of activity and CO conversion was calculated on that basis (Fig. 8). Analysis of the recorded IR spectra showed that a process of dehydroxylation occurred with temperature increase to cause a gradual decrease in intensity of the bands above 3000 cm^{-1}. Bands at 3350 and 3500 cm^{-1} appeared in the case of the SIGP sample at 100 °C. They were also stable at higher temperatures. In the case of Lieske sample a sharp decrease in intensity of the wide band around 3000 cm^{-1} was registered at 250 °C. This was accompanied by disappearance of the maximum positioned at 3150 cm^{-1} that is characteristic of γ-FeOOH phase. This change is assigned to γ-FeOOH phase transformation. In the experiment carried

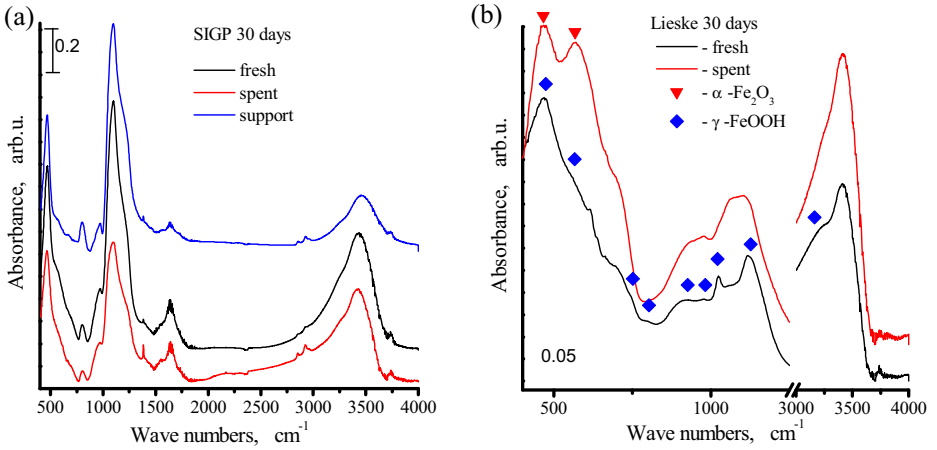


Fig. 6 Infrared spectra of biogenic materials before and after catalytic test: (**a**) SIGP and (**b**) Lieske feeding media

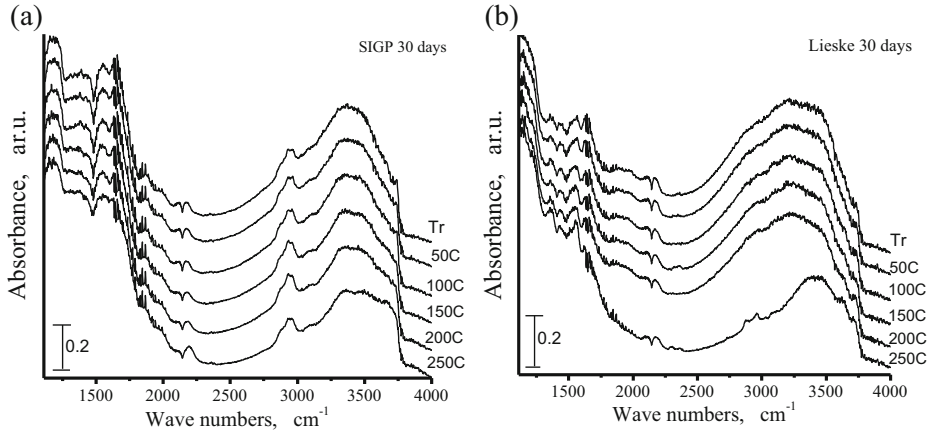


Fig. 7 *In situ* collected diffuse-reflectance infrared spectra in the reaction of CO oxidation on SIGP (**a**) and Lieske biomass (**b**)

out in presence of Lieske sample, gas phase CO bands slightly changed the symmetry of the wings in the whole course of reaction study and they decreased upon increasing reaction temperature. In contrast, the SIGP material showed stronger changes in the symmetry of the CO band wings at a temperature above 50 ºC. This asymmetry indicates a material transformation, which was confirmed by the spectrum recorded after purging the measuring cell from reaction mixture. A band at 2218 cm^{-1} was registered that had been overlapped by the Q-wing of CO bands.

Upon raising the reaction temperature, an increase in intensity of the characteristic bands below 1650 cm^{-1} due to carbonate groups/species was registered with both samples. During the catalytic test with a SIGP sample the band at 1550 cm^{-1} increased at 250 °C. The same band had a higher intensity in the range 150-250 °C in the case of Lieske sample. The band

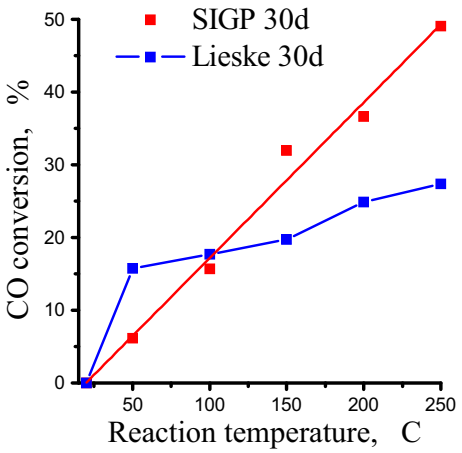


Fig. 8 CO conversion vs. reaction temperature

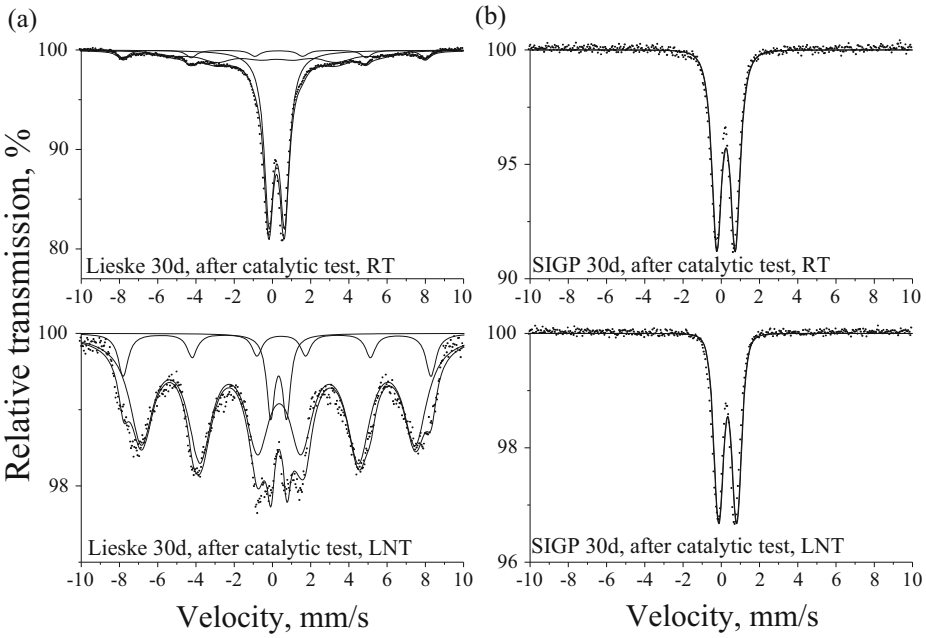


Fig. 9 Room temperature Mössbauer spectra of biogenic materials after catalytic tests: (**a**) Lieske and (**b**) SIGP feeding media

at 1400 cm^{-1} also increased its intensity at 250 °C. These changes could be attributed to an increase of the amount of different carbonate forms/species and their rearrangement on the samples' surface. CO_2 release as reaction product was registered by the presence of a band at 2340 cm^{-1} at $\geq$150 °C in the case of Lieske sample. A band due to CO_2 gaseous phase was not registered with SIGP sample (or its intensity is low). This special feature assumes CO depletion with formation of surface carbonate species, which are stable under reaction conditions. Taking into account the appearance of the 2218 cm^{-1} band, a transformation of

SIGP biomass composition is supposed. This process is not completed in the range of used reaction temperatures and it is in conformity with a constantly increasing CO conversion (Fig. 8).

Spent samples were studied by transmission IRS. Spectra are shown on Fig. 6. The spectrum of SIGP sample does not give clear information about iron-containing phase because of SiO_2 presence and its intensive bands overlap the characteristic bands of iron oxide compounds. Changes of composition were registered in a spectrum of spent Lieske material. The characteristic bands of lepidocrocite disappeared and typical bands of hematite appeared at 567 and 469 cm^{-1}. Thus, the observed change in composition of Lieske sample during in situ studied CO oxidation at 250 °C could be assigned to γ-FeOOH $\rightarrow$ α-Fe_2O_3 transition.

RT and LNT Mössbauer spectra of spent biogenic samples after catalytic tests (Fig. 9) reveal a change of phase composition and dispersity in the case of a sample from Lieske cultivation media. Two sextet components were registered. They have the characteristic parameters of α-Fe_2O_3 and γ-Fe_2O_3 (Table 2). Therefore, phase transformations of iron oxihydroxides toward oxides were registered in the material. According to previous investigations on CO oxidation activity of biogenic iron oxides/hydroxides this phase transformation is responsible for a registered lower CO conversion in presence of Lieske biomass [15]. The relative area of the doublet component, which was presented in the RT spectrum of this sample strongly decreased with a temperature decrease: from 63% (RT spectrum) to 7% (LNT spectrum). This indicates that SPM γ-Fe_2O_3 with nanometric size is the main presented phase in this sample [19]. Both RT and LNT Mössbauer spectra as well as the calculated parameters after their evaluation (Table 2) show no differences in phase composition or dispersity in the case of tested biomaterial prepared in SIGP feeding media. This could be explained by a stabilizing role of larger silicon amount in the cultivation solution [9, 12].

4 Discussion and conclusions

Dynamics of different phase formation and morphology changes were followed by comparison of series of iron-based biogenic powder materials and biofilms prepared by cultivation of *Leptothrix* group bacteria in different type feeding media: Lieske and silicon-iron-glucose-peptone. Samples at an early stage of biomaterial preparation (4 days), intermediates (10, 21 days) and after achieving a constant composition for 30 days were studied. Applied characterization methods reveal the role of silicon content in media composition and the impact of biofilm preparation on a SiO_2@Al plate on the morphology, stability, and catalytic properties of the materials in CO oxidation. The presence of nucleation sites on the surface of used support also strongly influence the mechanism of biotic Fe^{2+} oxidation and the formation of a variety of iron species. Comparative analysis of the obtained materials showed differences in phase composition, stability and dispersity of the biogenic powder material and biofilms. Changes were found to occur during the cultivation period and during the catalytic tests (registered by in situ DRIFTS) in the case of Lieske feeding media. On the other hand, no differences were registered in biogenic powders and biofilms when SIGP nutrient medium was used for bacteria cultivation neither in studied period nor after catalytic tests. This could be regarded to the influence of extra silicon content in the feeding media in this case and its stabilizing effect on the formed biomaterial. These results are very important for further application of the studied biogenic materials as catalysts. Formation of iron oxihydroxide nanotubes was established also in this case, which gives prospects for further investigation of this biomaterial for other practical applications (e.g. in electronics).

In this case, the major factor that affects both the stability and the properties of the products is Si content in pristine biomaterial structure. Silicate stabilizes the structure and hampers its conversion to different polymorphs toward hematite as end compound. The presence of Si hinders the formation of dissolution–oxidation–precipitation products and inhibits the crystallization and growth of the pre-formed iron compounds in the subsequent transformation stage [9, 12].

During the study, important information about phase composition, dispersity and magnetic properties of prepared and tested biomaterials was collected using RT and LNT Mössbauer analysis. Formation of tetrahedrally coordinated Fe(III) ions on a SiO_2@Al plate was registered in both studied feeding media. The amount of these Fe(III)-tetra species decreased with increasing the cultivation time.

The *Leptothrix* genus of bacteria could be used for selective production of (oxi)hydroxide biogenic materials of high dispersion. The biomass separation process was improved by the use of appropriate support. The support also moderated the chemical oxidation rate of the Fe^{2+} ions and adjusted the conditions for preparation of iron (oxi)hydroxide nanotubes. The studied biogenic preparation method has a numerous advantages as a green and sustainable method of preparation of advanced nanosized materials which could be successfully used as catalysts.

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