

Comparative analysis of the catalytic behaviour in CO oxidation of iron containing materials obtained by abiotic and biotic methods and after thermal treatment

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This work concerns synthesis of iron oxide containing materials by biotic and abiotic methods and comparison of their properties aimed at finding a common point of intersection that may determine a possible replacement of abiotic materials. Biosynthesis comprised *Leptothrix* genus of bacteria cultivation in growth medium of Adler. Thermal treatment of biomass samples was used in order to approximate synthesis conditions of the biogenic iron oxide material to those of abiotically obtained hematite. The catalytic activity of the samples was measured in the reaction of CO oxidation by two ways: *in situ* infrared spectroscopy using a diffuse-reflectance measuring chamber of Nicolet 6700 spectrometer high-temperature vacuum accessory and a flow-type glass reactor. Biomass showed low CO conversions up to 200°C but an increase at 250°C was registered by both used methods. This increase was accompanied by phase transformation. Initial catalytic activity was a result of predominant work of lepidocrocite, whereas a higher activity at 250°C was due to formed maghemite. Abiotic hematite was a bit more active below 240°C than a thermally treated biomass sample in flow-type glass reactor experiments. At higher temperatures, both materials demonstrated the same CO conversion. Spent samples did not show any changes of composition. Although the studied samples were synthesized by different methods, which resulted in different original iron oxide phases, their catalytic performance was very close. Thermally treated biomass samples (obtained by cultivation in Adler's medium) could replace chemically obtained iron oxide as a catalyst in the studied reaction.

Keywords: biogenic iron-containing material, *Leptothrix* genus of bacteria, CO oxidation, *in situ* diffuse-reflectance infrared spectroscopy, chemically synthesized iron oxide.

INTRODUCTION

Iron oxide compounds are widely used in catalysis as active components or as ingredients that improve performance of other catalytically active materials. Various methods are used for their synthesis. Chemical methods use toxic substances, consume much energy, and produce hazardous waste solutions. [1–5]. Despite these drawbacks the obtained products are of good purity and, usually, have well-defined properties. In nature, iron oxide and iron hydroxide compounds are obtained owing to iron biomineralization. Bio-inspired technologies are aimed at imitating these processes by inclusion of different mediators like microorganisms and phytochemicals. These methods are realized at ambient pressure and temperature and manifest ecology friendly features [3,4,6–15]. However, the obtained products exhibit a multicomponent character.

This work is aimed at comparing the properties of iron oxide containing materials, synthesized by biotic and abiotic methods, in order to find a common point of intersection that will determine a possible substitution of the abiotic materials.

EXPERIMENTAL

Magnetite, Fe₃O₄, was synthesized by a chemical route in which FeSO₄ and Fe(NO₃)₃ solutions were mixed, purged for 30 min with N₂ and then precipitated by addition of NaOH solution at pH = 13.5. The obtained precipitate was washed with distilled water and ethanol and dried at 70°C. The synthesized Fe₃O₄ was calcined at 450°C for 2 h to be converted into a stable form of iron oxide.

Biogenic iron-containing material was supplied by Prof. V. Groudeva and coworkers from the Faculty of Biology at St. Kliment Ohridski University of Sofia. Biosynthesis has been performed by a six-month cultivation of bacteria from *Leptothrix* genus in growth medium of Adler. In the literature, it is referred to a medium that is suitable for cultivation of *Sphaerotilus-Leptothrix* group of bacteria [16]. Obtained biomass has been separated by decantation of the liquid, washed by distilled water, and dried at 40°C.

The catalytic activity of the samples was studied in a test reaction of CO oxidation. Experiments with the biogenic material were performed in two different ways. One of them involved reaction in a high-temperature vacuum chamber (HTVC) accessory of

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Nicolet 6700 spectrometer and was monitored *in situ* by diffuse-reflectance (DR) infrared spectroscopy. Before catalytic measurement the sample was subjected to a surface cleaning procedure in a flow mixture (40 ml.min⁻¹) of N₂+O₂ (25 vol.% O₂) at temperatures up to 200°C. Further, the measurements were performed using a gas flow mixture of 88 ml.min⁻¹ (9 vol.% CO, 11.4 vol.% O₂, N₂) at various reaction temperatures (100, 150, 200, 250°C) at a heating rate of 10 deg.min⁻¹ and a 30-min soak at each attained level. This procedure was used in order to achieve constant parameters of the studied system (constant infrared spectra for selected conditions). The second mode considered the CO oxidation reaction in a flow-type glass reactor (FTGR) with 0.3-cm³ samples (mesh of 0.63–0.8 mm). CO conversion was followed by a Hewlett Packard 5890 Series II gas chromatograph. Elapsed time to attain steady state working conditions was different depending on the reaction temperature (50, 100, 200, and 250°C). To approximate synthesis conditions of the biogenic iron oxide material to the chemically obtained counterpart, the biomass sample was pretreated in the glass reactor using a flow mixture of 1760 ppm CO, 0.92 vol.% O₂, and N₂ at a GHSV of 40000 h⁻¹ from ambient temperature to 300°C. The latter composition of the flow mixture was further used for catalytic tests of both samples. Such a preconditioning was assumed applicable to compare the catalytic properties of both the biogenic and synthetic materials.

All 'as synthesized' biomass samples, thermally treated and spent after catalytic tests, were studied by transmission infrared spectroscopy in the far and middle regions using KBr pellets containing 0.5 or 1% of studied substance. Spectra were recorded on the same spectrometer.

RESULTS AND DISCUSSION

Spectra of biomass obtained after cultivation of *Leptothrix* genus of bacteria (Fig. 1a) show bands characteristic of γ -FeOOH at 277, 371, 398, 474/480, 560, 748, 882, 1022, and 1152 cm⁻¹ [17–21]. However, the spectral features direct also to the presence of some γ -Fe₂O₃ (broad bands at about 398 and 560 cm⁻¹ and a shoulder at about 330 cm⁻¹) and α -FeOOH (bands positioned at about 277, 398, 882, and ~3152 cm⁻¹) [17–21]. The analysis allows claiming that the biomass contains lepidocrocite (γ -FeOOH) as a predominant phase with some amounts of hematite (α -Fe₂O₃) and maghemite (γ -Fe₂O₃). In a previous study of biomass obtained by cultivation of *Leptothrix* bacteria in various cultivation media [22,23] γ -FeOOH has been found

as an essential component in an iron-containing material formed in Adler's medium by Mössbauer spectroscopy and XRD.

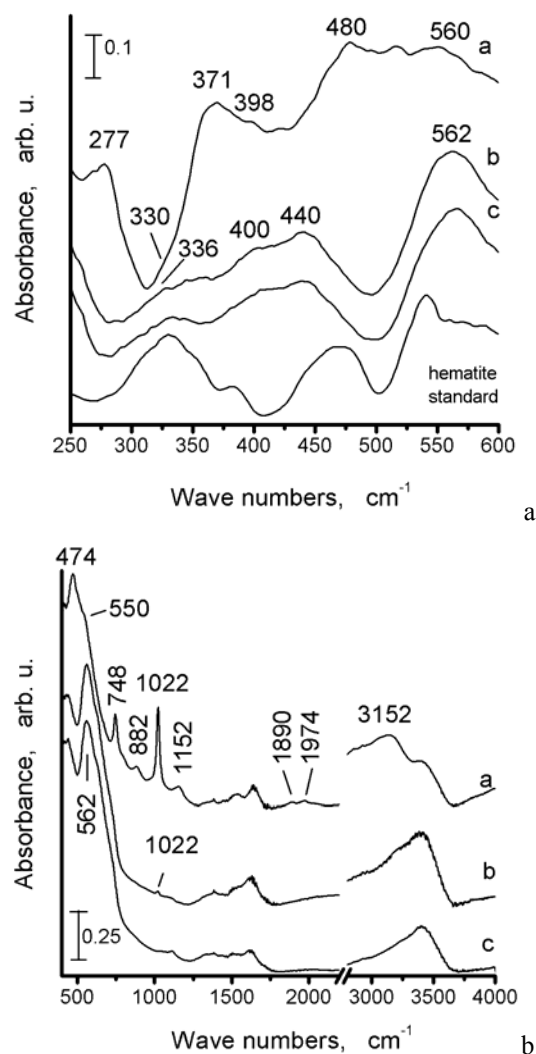


Fig. 1. Transmission infrared spectra of a biomass sample in the far (a) and middle (b) regions: a – fresh biomass sample; b – spent sample after catalytic measurements in the high-temperature vacuum chamber; c – spent sample after a catalytic test in a flow type reactor.

In situ DR spectra recorded during the reaction of CO oxidation over a biomass sample (Fig. 2) disclose bands at 1890, 1974, and 3209 cm⁻¹ characteristic of iron oxide/oxyhydroxide structures and the characteristic doublet of CO in the reaction system with a minimum centred at 2142 cm⁻¹ [23]. Integrated intensity of the CO bands was accepted as a measure of catalytic activity of the studied samples in this set of experiments. It decreased on increasing the reaction temperature (Fig. 3, HTVC). The decrease in integrated band intensity of the gas phase CO amount was about 40% at 250°C. The changes were accompanied by a decrease and disappearance of the bands at 1890 and 1974 cm⁻¹,

as it is seen in figure 2 in the spectrum taken at 250°C. Changes during the course of the catalytic reaction at 250°C are in accordance with a phase transition process $\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3$ [21].

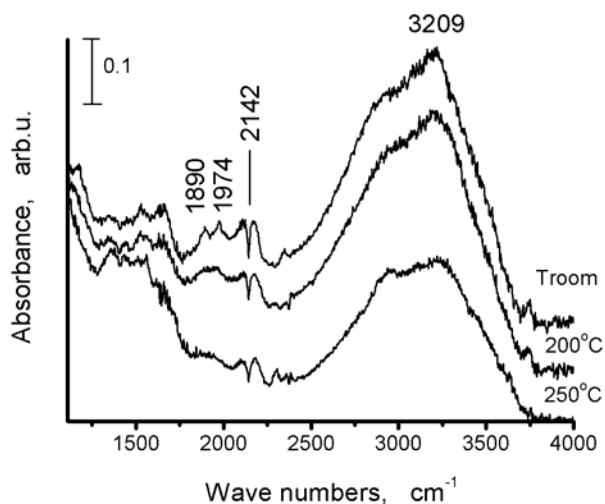


Fig. 2. *In situ* diffuse-reflectance infrared spectra of a biomass sample recorded at different reaction temperatures.

Spectra of the spent sample (Fig. 1b) confirm the phase transformation. The bands at 336, 400, and 562 cm^{-1} are characteristic of maghemite $\gamma\text{-Fe}_2\text{O}_3$ [17]. Bands at 336 and 562 cm^{-1} propose also presence of hematite $\alpha\text{-Fe}_2\text{O}_3$. Formation of these modifications of the iron oxide is expected as the initial sample contains $\alpha,\gamma\text{-FeOOH}$ that is converted into the respective oxides under such conditions [21]. The presence of some unconverted lepidocrocite should not be excluded because of the wide band at 440 cm^{-1} and that of very low intensity at 1022 cm^{-1} .

Catalytic measurements of biomass samples obtained by the both used technical methods showed a low CO conversion up to 200°C and an increase at 250°C (Fig. 3). This increase was accompanied by phase transformation that started at 200°C and continued at higher temperatures, as evidenced by the infrared spectra displayed in figure 2. Bearing in mind the different reaction conditions of applied experimental setup for examination of the catalytic properties of the biomass, the conversion of carbon monoxide registered at 250°C should be related to sample composition by the end of the process of phase transformations. Analysis of the spectra of biomass tested in the HTVC shows the presence mainly of maghemite and small amounts of hematite and lepidocrocite. After reaction for 150 min in the flow-type glass reactor (FTGR, Fig. 3) the biomass contained mainly maghemite and some amount of hematite (larger than that of HTVC experiment) and lepidocrocite. The far IR spectrum of a spent sample after catalysis in the flow-type reactor (Figs. 1a,c)

resembles that of a spent biomass sample after a catalytic test conducted in the diffuse-reflectance accessory (Figs. 1a,b). However, the former suggests the presence of a bit higher amount of hematite taking into account the increased intensity of the band at about 336 cm^{-1} and broadening of the band at 562 cm^{-1} . These results allowed us to accept that the chemical composition of the studied biomass samples was the same or nearly coincided with that resulted at 250°C under the reaction conditions used in both types of experiments.

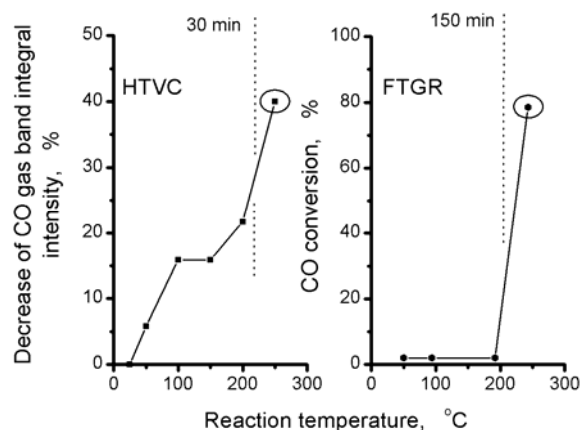


Fig. 3. Change of catalytic activity in dependence of reaction temperature: HTVC – evaluated by a decrease of integral CO gas band intensity; FTGR – CO conversion.

Abiotic magnetite and biomass samples were thermally treated before examination in the flow-type glass reactor. The aim of this pretreatment was to obtain a relatively stable sample composition and to approximate to some extent the conditions of material preparation, which is a prerequisite for their comparative study. Infrared spectra of ‘as synthesized’ and calcined abiotic iron oxide are displayed in figure 5. Spectrum ‘a’ confirms that the obtained iron oxide is magnetite (bands at 398, 455, and 576 cm^{-1}). Spectrum ‘b’ shows bands at about 310, 385, 462, and 540 cm^{-1} , all characteristic of hematite [10, 21]. The result indicates that calcination of the magnetite at 450°C for 2 h is sufficient to convert this compound in a most stable form. Thermally treated biomass produced an infrared spectrum with bands located at about 333, 408, 440, and 565 cm^{-1} (Fig. 4a). Their intensity and position correspond to those of the spent biomass samples after HTVC and FTGR catalytic tests (Figs. 1a,b) and (Figs. 1a,c), respectively. These features correspond to a complex composition of the thermally treated biomass containing maghemite, hematite, and lepidocrocite. Maghemite is still the predominant phase, while hematite and traces of unconverted lepidocrocite exist together with the main phase as it is shown for mentioned spent samples.

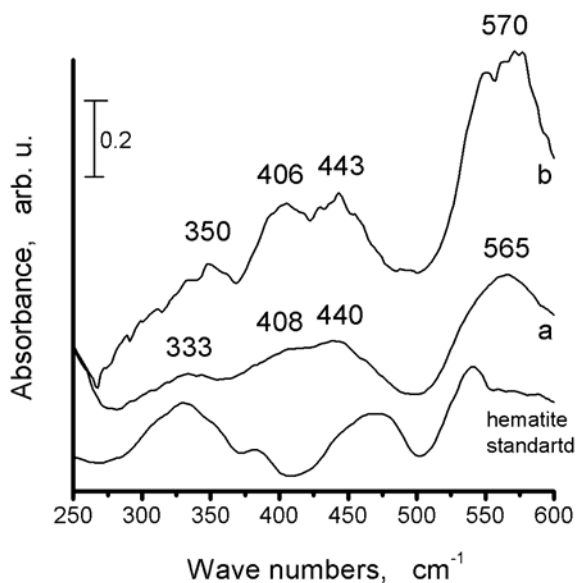


Fig. 4. Far-IR transmission spectra of biomass samples: a – thermally treated biomass sample; b – thermally treated biomass sample after catalytic test.

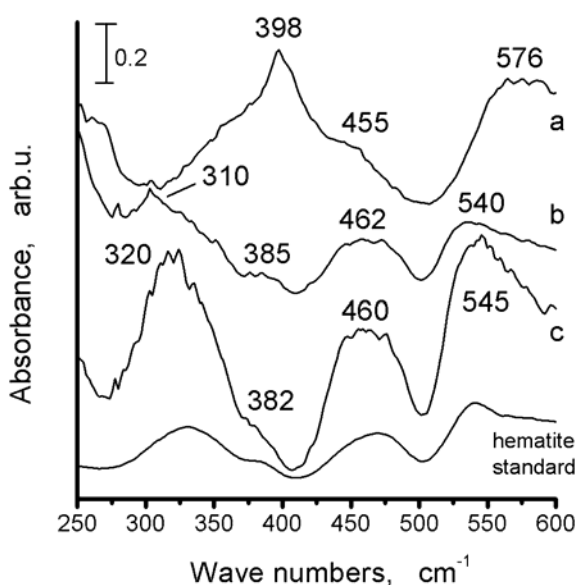


Fig. 5. Far-IR transmission spectra of abiotically synthesized iron oxide: a – ‘as synthesized’ sample (Fe_3O_4); b – after calcination of abiotic sample at 450°C for 2 h ($\alpha\text{-Fe}_2\text{O}_3$); c – calcined abiotic sample after catalytic test in a flow-type reactor.

Catalytic measurements of abiotic hematite and a thermally treated biomass sample in the flow-type glass reactor showed that at temperatures below 240°C the abiotic sample is a little bit more active. Both materials demonstrate the same CO conversion level in the reaction of CO oxidation at temperatures higher than 240°C (Fig. 6). Spectra of spent samples after the catalytic tests did not show any changes under reaction conditions (cf. spectra ‘a’ and ‘b’ in Fig. 4 and spectra ‘b’ and ‘c’ in Fig. 5). Despite the different methods of sample synthesis that result in

different original iron oxide phases, the catalytic performance in the reaction of CO oxidation is very close.

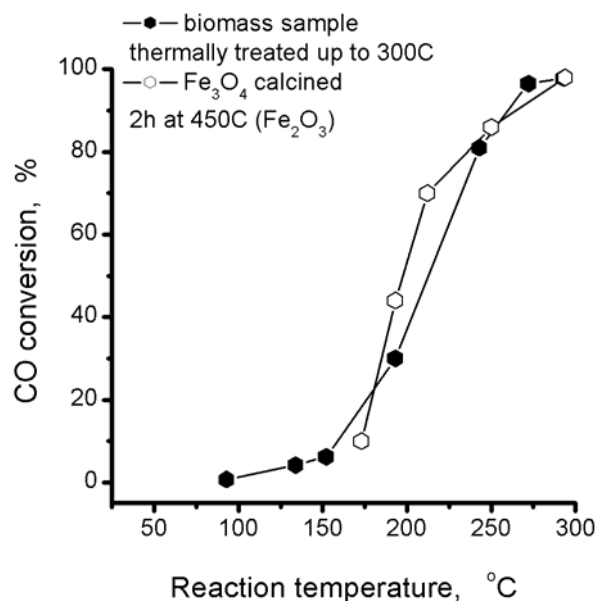


Fig. 6. Catalytic performance of biogenic iron-containing sample and abiotic hematite in the CO oxidation reaction registered using a flow-type glass reactor.

In conclusion, it should be noted that: (i) the catalytic activity up to 200°C of biotically obtained iron-containing material in the reaction of CO oxidation is a result of predominant work of lepidocrocite, but the increase in activity at 250°C is due to formed maghemite; (ii) a biogenic material thermally treated at 300°C is composed of maghemite, hematite, and lepidocrocite and showed almost the same catalytic activity in the reaction of CO oxidation like abiotically obtained hematite; (iii) both biogenic and abiotic thermally treated samples preserved their composition during the catalytic tests; (iv) thermally treated biomass, prepared by *Leptothrix* genus of bacteria cultivation in Adler’s growth medium, could replace chemically obtained iron oxide as a catalyst in the studied reaction.

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REFERENCES

1. K. B. Narayanan, N. Sakthivel, *Adv. Colloid Interface Sci.*, **156**, 1 (2010).
2. H. Jung, J.-W. Kim, H. Choi, J.-H. Lee, H.-G. Hur, *Appl. Catal. B-Environ.*, **83**, 208 (2008).
3. B. Kazprzyk-Hordern, M. Ziolk, J. Nawrocik, *Appl. Catal. B-Environ.*, **46**, 639 (2003).
4. A. B. Seabra, P. Haddad, N. Duran, *IET Nanobiotechnol.*, **7**, 90 (2013).
5. T. Shahwan, S. Abu Sirriah, M. Nairat, E. Boyaci, A. E. Eroglu, T. B. Scott, K. R. Hallam, *Chem. Eng. J.*, **172**, 258 (2011).
6. H. Hashimoto, S. Yokoyama, H. Asaoka, Y. Kusano, Y. Ikeda, M. Seno, J. Takada, T. Fujii, M. Nakanishi, R. Murakami., *J. Magnet. Magnet. Mater.*, **310**, 2405 (2007).
7. T. Sakai, Y. Miyazaki, A. Murakami, N. Sakamoto, T. Ema, H. Hashimoto, M. Furutani, M. Nakanishi, T. Fujii, J. Takada, *Org. Biomol. Chem.*, **8**, 336 (2010).
8. B. Xin, D. Zhang, X. Zhang, Y. Xia, F. Wu, S. Chen, L. Li, *Bioresour. Technol.*, **100**, 6163 (2009).
9. J. A. Rentz, I. P. Turner, J. L. Ullman, *Water Res.*, **43**, 2029 (2009).
10. R. Cornell, U. Schwertmann, *Iron Oxides*, Wiley-VCH Verlag, Weinheim, Germany, 2003.
11. R. W. Fitzpatrick, R. Naidu, P. G. Self, in: *Bio-mineralization Processes of Iron and Manganese - Modern and Ancient Environments*, Catena Supplement 21, (H. C. W. Skinner, R. W. Fitzpatrick, Eds.), Catena Verlag, Reiskirchen, Germany, 1992, p. 263.
12. D. A. Ankrah, E. G. Sogaard, in *13th Int. Water Technol. Conf., IWTC 13, 2009*, Hurghada, Egypt, p. 999.
13. T. Ema, Y. Miyazaki, I. Kozuki, T. Sakai, H. Hashimoto, J. Takada, *Green Chem.*, **13**, 3187 (2011).
14. A. Alharthi, R. A. Blackley, T. H. Flowers, J. S. J. Hergreaves, I. D. Pulford, J. Wigzell, W. Zhou, *J. Chem. Technol. Biotechnol.*, (2014), doi:10.1002/jctb.4434.
15. G. E. Hoag, J. B. Collins, J. L. Holcomb, J. R. Hoag, M. N. Nadagouda, R. S. Varma, *J. Mater. Chem.*, **19**, 8671 (2009).
16. D. Ellis, *Microbiology of the Iron-depositing Bacteria*, Wexford College Press, Palm Springs, CA, 2003.
17. A. U. Gehring, A. M. Hofmeister, *Clays and Clay Minerals*, **42**, 409 (1994).
18. N. Lazaroff, W. Sigal, A. Wasserman, *Appl. Environ. Microbiol.*, **43**, 924 (1982).
19. S. Music, A. Saric, S. Popovic, K. Nomura, T. Sawada, *Croat. Chem. Acta*, **73**, 541 (2000).
20. B. Weckler, H. D. Lutz, *Eur. J. Solid State Inorg. Chem.*, **35**, 531 (1998).
21. R. M. Cornell, U. Schwertmann, *The Iron Oxides. Structure, Properties, Reactions, Occurrences and Uses*, Wiley-VCH Verlag, Weinheim, 2003.
22. M. Shopska, Z. Cherkezova-Zheleva, D. Paneva, M. Iliev, G. Kadinov, I. Mitov, V. Grudeva, *Nanoscience & Nanotechnology*, Vol. 13, (Proc. 14th Workshop on Nanostructured Materials Application and Innovation Transfer, 2013, Sofia), Eds. E. Balabanova, E. Mileva, Bulgarian Academy of Sciences, Sofia, 2013, p. 31.
23. L. H. Little, *Infrared spectra of adsorbed species*, Academic Press, London, 1966.

СРАВНИТЕЛЕН АНАЛИЗ НА КАТАЛИТИЧНОТО ПОВЕДЕНИЕ В ОКИСЛЕНИЕ НА СО НА ЖЕЛЯЗО-СЪДЪРЖАЩИ МАТЕРИАЛИ ПОЛУЧЕНИ С АБИОТИЧНИ И БИОТИЧНИ МЕТОДИ И СЛЕД ТЕРМИЧНА ОБРАБОТКА

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(Резюме)

Изследването е свързано с получаване чрез биологичен или небиологичен метод на материали съдържащи железен оксид и сравняване на техните свойства за да се намери пресечна точка определяща възможност за заместване на абиотичните материали. Биологичният синтез включва култивиране на бактерия от рода *Leptothrix* в среда на Адлер. Използвана е термична обработка на образец от биомаса за наподобяване на условията на синтез на биогенния железен оксид на тези на получаване на небиогенен хематит. Каталитичната активност на образците е измерена в реакцията на окисление на СО по два начина – чрез „ин ситу“ дифузно-отражателна инфрачервена спектроскопия в кювета за изследване при висока температура и в стъклен реактор от проточен тип. И при двата метода на изследване биомасата показва ниска конверсия на СО при температури до 200°C, но се регистрира повишение при 250°C. Нарастването на активността е съпроводено от промяна във фазовия състав. Началната каталитична активност е резултат от преобладаващ принос на лепидокрокита, докато по-високата активност при 250°C се дължи на образуването на магхемит. Експериментите проведени в проточен реактор показаха, че при температура под 240°C абиотичният хематит е малко по-активен от термично обработения образец от биомаса. Двата вида материали показаха една и съща конверсия на СО при по-високи температури. Съставът на отработените образци не се различава. Въпреки, че изследваните образци са синтезирани по различен начин, водещ до различни начални фази от железни оксиди, каталитичните им свойства са много близки. Термично обработени биогенни образци, получени чрез култивиране на бактериите в среда на Адлер, биха могли да заместят като катализатор за изследваната реакция железен оксид получен чрез химичен синтез.