



Rico, J.L., and Hargreaves, J.S.J. (2017) Synthesis and characterization of iron and iron nitride microtubes obtained from biogenic iron oxide. *Journal of Materials Science*, 52(9), pp. 5188-5193. (doi:[10.1007/s10853-017-0759-5](https://doi.org/10.1007/s10853-017-0759-5))

This is the author's final accepted version.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/133961/>

Deposited on: 11 January 2017

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk33640>

Synthesis and characterisation of iron and iron-nitride microtubes obtained from biogenic iron oxide

J. L. Rico¹, J. S. J. Hargreaves²

¹Laboratorio de Catálisis, Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, México.

²WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK.

E-mails: Justin.Hargreaves@glasgow.ac.uk; jlrico@umich.mx

Abstract

Purpose

With the aim to obtain iron tubular microstructures attractive for various applications, we have used a natural biogenic iron ochre as a raw material and explore various procedures and experimental conditions to achieve our goal.

Methods

Our experiments included reduction, nitridation and characterisation of microtubes derived from biogenic iron ochre. Various temperatures of reduction under streams of H₂/N₂ or NH₃ were tested.

Results

Our results show that the tubular structure is maintained after reduction of the natural material under H₂/N₂. In addition, ammonia was not produced under our experimental conditions, and as expected, hydrogen reduced the material. However, the treatment under NH₃ reduces the material and allows the incorporation of nitrogen into the structure of the solid yielding iron nitride microtubes.

Conclusions

Reduced and nitrated microstructures were successfully obtained from natural biogenic iron ochre. A temperature of 500 °C seems to be suitable to expose the calcined biogenic iron ochre under H₂/N₂ for 4 h or under ammonia for 8 h to obtain reduced or nitrated microtubes, respectively. The stability of the tubular structure during reduction/reduction-nitridation is maintained under both treatments. Further interesting applications of this natural biomaterial could be envisaged.

Keywords: biogenic iron oxide, reduction, nitridation

Introduction

Biogenic iron oxide can be of interest in a wide range of applications, for instance, as adsorbents for the removal of pollutants [1, 2]; and in the field of heterogeneous catalysis. In the latter respect, Hargreaves and Alharthi [3] recently reviewed and highlighted some interesting examples on the production and application of biogenic and biomorphic materials. In another study, Alharthi et al. [4] reported the use of tubular biogenic iron oxide for the cracking of methane, to obtain hydrogen and a magnetic carbon coated solid. The authors reported that a small amount of CO in addition to hydrogen was produced in the temperature range of 600 to 800 °C. They also observed that the deposited carbon covers the iron species and forms filaments. Hishimoto et al. [5] have used biogenic iron oxide source to obtain silica by dissolving iron oxide using hydrochloric acid. The resulted material with strong Brønsted and Lewis acid sites, showed better activity than conventional silica for the ring opening of epoxides and Friedel–Crafts-type alkylations. Mandai et al. [6] reported the use of biogenic iron oxide as support for the synthesis of Pd catalysts which were then evaluated in the solvent-free Suzuki–Miyaura coupling reaction. They found that the natural material can be used effectively as support for this purpose. Shopska et al. [7] have obtained iron-containing material from cultivation of *Leptothrix* genus bacteria in various growth media. The powder was characterised and evaluated as catalyst in the oxidation of CO. Good catalytic activity was observed at temperatures higher than 250 °C which was attributed to the transformation of iron oxyhydroxides to γ -Fe₂O₃. In another study, Shopska et al. [8] have synthesized Pd/Al-Si-O and Fe-Pd/Al-Si-O catalysts. The former was prepared by the sol-gel route and the latter by immersing this sample into a glucose-peptone elective medium containing *Leptothrix* genus bacteria and

iron. The authors concluded that both catalysts show similar activities for the CO oxidation independently of the presence of iron. In another study reported by Ema et al. [9] the surface of a dried and calcined biogenous iron oxide was modified with silane coupling agents to obtain organic–inorganic hybrid materials. The solids were then used as supports for enzymes. The authors reported that the best activity for the resolution of secondary alcohol in *i*-Pr₂O was observed for *Burkholderia cepacia* lipase immobilized on the organic–inorganic hybrid materials prepared by modifying the dried biogenous iron oxide with 3-methacryloxypropyltrimethoxysilane. Additionally, Ema et al. [10] studied the synthesis of cyclic carbonates from epoxides and CO₂ under solvent-free conditions. Metalloporphyrins immobilized on biogenic iron oxide were used as catalysts for this reaction. They observed high catalytic activity and reusability of the catalyst of 0.1 mol% loading.

In order to further explore the possibilities of use of the biogenic iron oxide, the aim of the present work was to study the reduction and nitridation of this natural material trying to preserve the tubular morphology. For this purpose, the iron source was treated under streams of N₂/H₂ or NH₃ at different temperatures and experimental conditions.

Experimental

The collection point of iron ochre was a stream in Douglaston, Milngavie, UK. The gelatinous sludge was first vacuum-filtered and washed with deionized water three times. The resulted sludge was then dried overnight in air at 75 °C and finally calcined under a flow of air from ambient temperature to 600 °C at 10 °C/min and a dwell of 5 h was applied at the final temperature. The natural material was then ready for reduction, nitridation and further characterization.

With the aim to reduce and incorporate nitrogen into the structure, the samples were treated under N₂/H₂ or ammonia. In a typical experiment, 0.5 g of calcined material was placed in the middle of a tubular quartz reactor and held between two quartz-wool beds. When using N₂/H₂ (1:3 vol), 60 ml/min flowrate was used. All samples were heated from ambient temperature to the set point at 10 °C/min and a dwell of 4 h at the final temperature was applied. The reduction temperatures in presence of N₂/H₂ were conducted at 300, 400, 500 and 700 °C. After the dwell time, the materials were cooled down under N₂/H₂ and once at ambient temperature, the samples were carefully passivated in air. In order to check the possible formation of ammonia during the treatment with N₂/H₂, the outlet gas from the reactor was always bubbled into a H₂SO₄ solution and its conductivity was always measured.

A different experimental procedure was followed when ammonia was used as reductant. For this purpose, 0.5 g of calcined natural material was placed in the middle of a quartz reactor and treated under 100 ml/min of NH₃ from ambient temperature to the set point. The temperatures tested were 400, 450, 500, 550, 600 and 700 °C. In all cases a heating rate of 3°C/min and a dwell of 8 h at the final temperature were applied. After the dwell time, the powder was cooled down under ammonia and once at ambient temperature, the sample was finally passivated under 100 ml/min of N₂/O₂ (99:1 vol) and discharged from the reactor. The samples are labeled hereafter as H3, H4, H5 and H7, for samples treated under H₂/N₂ at 300, 400, 500 and 700 °C, respectively. Similarly, N4, N45, N5, N55, N6 and N7 for samples treated under ammonia at 400, 450, 500, 550, 600 and 700 °C, respectively.

All samples were finally characterized by various techniques. CHN determination was performed using an Exeter Analytical CE-440 elemental analyser. Surface areas were determined with a Micromeritics Gemini system by physisorption of N₂ at 77K by applying the BET equation. X-ray diffraction (XRD) patterns were collected using a Panalytical X'Pert PRO MPD diffractometer with Cu K α radiation. A 2 θ range between 5 and 85° was scanned using a counting rate of 45 s per step with a step size of 0.016°. For the morphological features of solids, SEM images were acquired using a XL30 ESEM Philips microscope operating at 20 kV.

Results and discussion

Table 1 shows the surface areas, carbon, hydrogen and nitrogen content of samples. The raw material is not magnetic and exhibits a high content of carbon matter. However, the calcined powder shows low carbon content and is magnetic, in agreement with the calcined biogenic iron oxide reported by Tadashi et al. [9]. Furthermore, calcination at 600 °C in a flow air was effective for the removal of organic matter, in agreement with the work published by Shopska et al. [11]. The formation of the iron oxide during calcination was accomplished with a slight change in the red colour compared to the raw dried powder. However, all samples treated under N₂/H₂ or NH₃ were black at the end of the experiment.

Table 1. Characterisation of biogenic iron oxide samples before and after exposing to N₂/H₂ during 4 h at various temperatures.

Sample	Temperature, °C	Weight, %			BET, m ² /g
		C	H	N	
Dried		17.62	0.75	1.90	-
Calcined		0.20	0.18	0.00	48
H3	300	0.20	0.20	0.00	46
H4	400	0.20	0.23	0.01	47
H5	500	0.24	0.03	0.00	39
H7	700	0.14	0.00	0.01	12

The variations in C and H contents found in Table 1 are likely due to the uneven properties of the natural material. It is also clear in this table that nitrogen was not incorporated into the structure of the solid even at 700 °C. In addition, ammonia was not detected in the outlet gas during the experiments with H₂/N₂. However, hydrogen gradually reduced the sample. Table 1 also exhibits that the specific surface area shows a maximum in the range of 300-400 °C and then decreased. The smallest area is observed for H7 due to sintering at 700 °C, as expected. Additionally to the C, N and H contents reported above for the natural material, small amounts of other constituents, such as Si, Al, Ca, Mn, O, and Fe were identified using a EDS detector attached to the SEM microscope.

Table 2 shows the characterisation of samples treated under ammonia. Although the surface areas change slightly from one temperature to another, there is a clear decline in the values as the temperature increase. The maximum area was noted at 400 °C. As anticipated, the lowest surface area was measured for sample treated at 700 C.

Table 2. Characterisation of biogenic iron oxide samples after the treatment with 100 ml/min of ammonia at various temperatures.

Sample	Temperature, °C	Weight, %			BET, m ² /g
		C	H	N	
N4	400	0.25	0.28	4.14	43
N45	450	0.19	0.27	6.72	36
N5	500	0.17	0.22	6.75	35
N55	550	0.21	0.11	6.75	31
N6	600	0.27	0.19	6.71	27
N7	700	0.16	0.17	6.67	23

The treatment of the natural material under ammonia incorporates nitrogen as function of temperature, as shown in the previous table. The lowest nitrogen content was observed at 400 °C, then increased at 450 °C and practically remain constant at higher temperatures, indicating that the maximum amount of nitrogen incorporated into the iron ochre was attained. The samples were also investigated by XRD. Figure 1 presents these patterns for dried and calcined samples. The dried material shows reflections assigned to silica (PDF 085-0795) at about 20.8 and 26.6 °2θ, whereas the calcined sample in addition to silica, shows some reflections appearing at about 30.3, 35.7, 43.4, 57.4 and 63 °2θ which can be ascribed to Fe₂O₃ (PDF 076-3169).

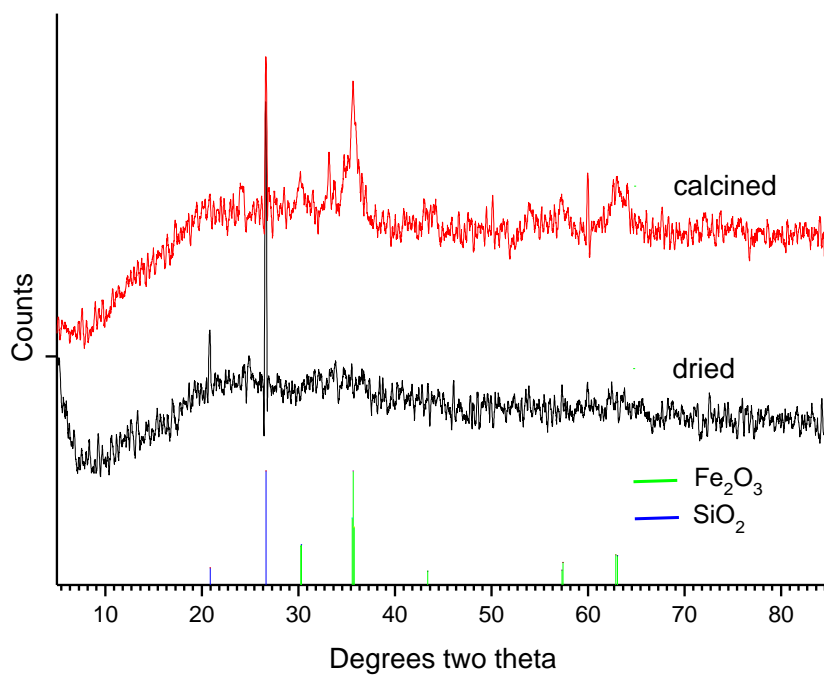


Figure 1. Diffraction patterns of the dried and calcined samples.

The XRD patterns of samples treated in N₂/H₂ at various temperatures are shown in Figure 2.

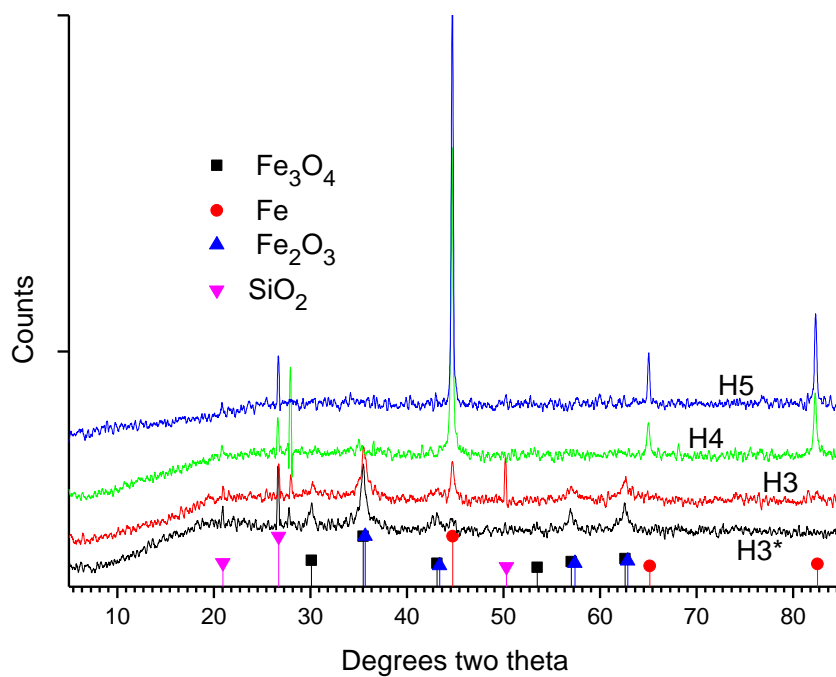


Figure 2. Diffraction patterns of samples after the treatment under 60 ml/min of N₂/H₂ (1:3 vol) during 4 h. Sample H3* was only kept 2 h at 300 °C.

Sample H3* conducted at 300 °C with a dwell of 2 h, shows a mixture of phases. Accordingly to database, the reflections at about 57 and 62.6 °2 θ are attributed to Fe₃O₄, (PDF 075-0033). However, since the diffractions are broad, it may also be possible to match Fe₂O₃ as shown in Figure 2. On the other hand, the experiment conducted at 300 °C during 4 h showed similar reflections of different intensity to those observed for H3* sample, but additionally, the peak at about 44.7 °2 θ which is assigned to iron (PDF 006-0696) was noticed. For samples treated at 400 °C and higher temperature, the patterns are similar and show reflections of different intensity assigned to iron metal at about 44, 65 and 82 °2 θ . The reflections at about 20.8 and 26.6 °2 θ present in all patterns are attributed to silica (PDF 087-2096). With the exception of silica which is segregated, the other elements detected by EDS, such as Si, Al, Ca and Mn, are apparently well distributed in the structure of the material. Although the patterns were taken after the treatment at high temperature, the reduction of iron species present in this source seems to follow the path Fe₂O₃ → Fe₃O₄ → Fe. However, our experimental procedure cannot rule out the formation of wüstite as intermediate, since the generation and transformation of this phase could occur during the reduction process. Jozwiak et al. [12] studied the reduction of pure iron compounds under H₂ and CO and reported that various partially-reduced species are possible to form accordingly to the experimental conditions. The authors observed by *in situ* XRD, the appearance of wüstite phase as an intermediate during the reduction of hematite in hydrogen at temperatures of reduction above 570 °C.

It has been reported by Volpe and Boudart [13] that the transformation of MoO₃ under ammonia leads to γ -Mo₂N which is pseudomorphic with the precursor. This observation is in agreement to the iron nitride obtained in our study by ammonolysis. Furthermore, we have also observed that the conversion of the iron oxide to reduced microtubes was also pseudomorphic under N₂/H₂. The presence of elements other than Fe in our natural material might also impart stability to the tubular structure during this process. The SEM micrographs presented in Figure 3 show that the microtubular structure is indeed retained at all tested temperatures. These images were taken from samples obtained at 500 °C and are representative of both treatments.

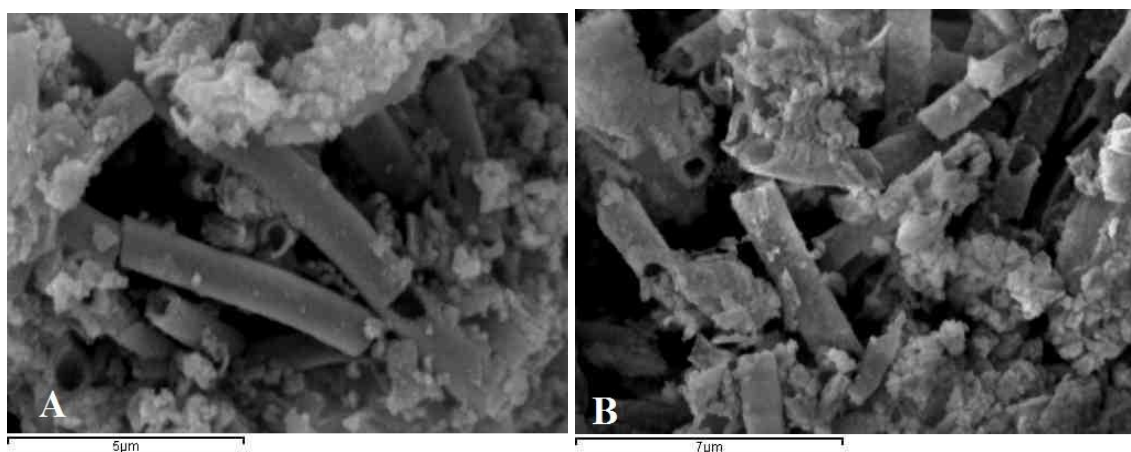


Figure 3. Iron nitride (A) obtained at 500 °C, and iron (B) microtubes reduced at 500 °C

Hideki et al. [14] have also reported that the tubular structure was maintained at high temperatures. However, the natural material was heated up in air and the structural changes were characterized by various techniques. They reported that even though the original tubular structure was retained when heating, the nanoscopic and local structures significantly changed. They have also found that the Fe-O-Si linkages were progressively cleaved when increasing temperature to finally produce α -Fe₂O₃/amorphous silicate at 800 °C. In our case, clear reflections assigned to silica was observed in our material even before treating under N₂/H₂.

It is interesting to comment that the reduced surface resulted from the treatment under N₂/H₂ was incapable to activate and incorporate nitrogen into the structure and it was therefore undetected by elemental analyser in the final solid. However, ammonia both reduces the material and incorporates nitrogen into the structure, yielding iron nitride microtubes. An SEM image of the nitrided sample is also presented in Figure 3. Additionally, the XRD patterns of the nitrided samples are presented in Figure 4. The reflections for sample N4 indicate the presence of magnetite (PDF 089-2355) at about 30, 35.4, 43, 56.9 and 62.5 °2 θ ; silica (PDF 075-0443) with characteristic reflections at about 20.8 and 26.6 °2 θ and reflections for Fe₂N (PDF 074-8392) at 40.7, 42.6, 56.5, 67.3, and 75.6 °2 θ indicating uncomplete reduction at those experimental conditions. However at 450 °C, the XRD pattern for N45 shows only reflections for ζ -Fe₂N (PDF 00-050-0958) and silica (01-087-2096) after 8 h under NH₃. According to the

searching, the patterns obtained at higher temperatures show characteristic reflections for Fe_2N (PDF 076-0090) and quartz (PDF 085-0794) (sample N5 and N55) and $\zeta\text{-Fe}_2\text{N}$ (PDF 050-0958) and $\alpha\text{-SiO}_2$ (PDF 087-2096) for N6. The change from orthorhombic, $\zeta\text{-Fe}_2\text{N}$ (PDF 050-0958), at 450 °C to hexagonal, Fe_2N (PDF 076-0090), at 500 and 550 °C, and then again to orthorhombic at 600 °C is unclear and unexpected.

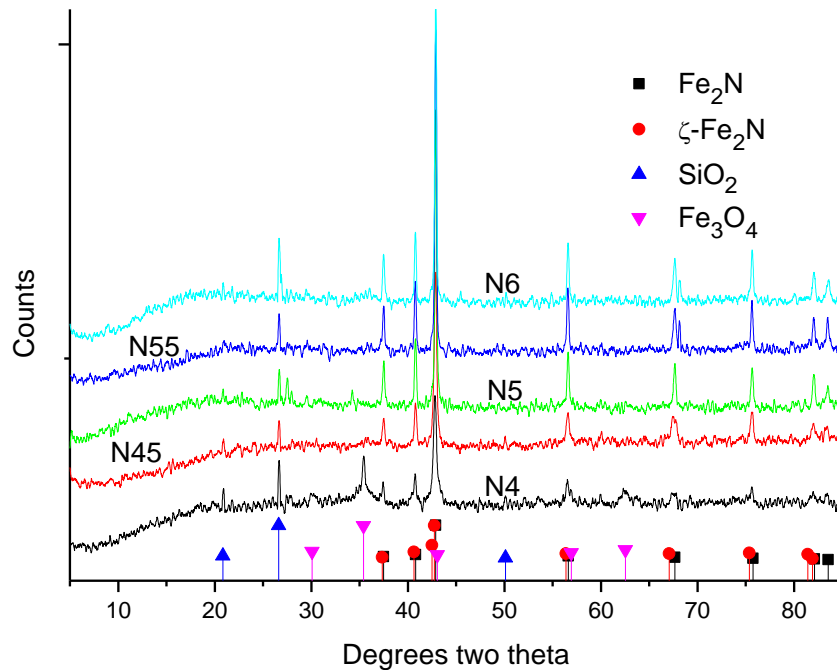
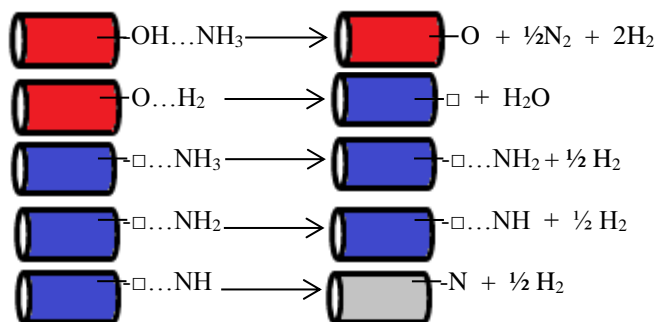


Figure 4. Diffraction patterns of samples treated under NH_3 .

Nitridation of the surface and dissociation of NH_3 to form N_2 and H_2 probably occur simultaneously as suggested by Darken and Gurry [15]. Intermediate nitrogenated species are likely the main species responsible for nitridation, since a nitride was not formed under N_2/H_2 . Adsorption and transformation of NH_3 on O, OH or/and vacancy, \square , on the surface of the solid could lead to nitridation. A possible pathway is the following:



In another published study, the nitridation of iron oxide particles of different sizes under ammonia was reported by Nishimaki et al. [16]. They found that decreasing the size of the iron particles, diminished the nitrogen content in the solid after nitridation and explained this behavior by assuming a greater dissociation activity of ammonia, compared to nitridation, when reducing the particle size. Greater dissociation of ammonia on iron nanoparticles implies high formation rates of N_2 and H_2 which were

inactive for nitridation. The latter observation is in agreement with our results when treating the natural material with N_2/H_2 as feed.

Conclusions

The synthesis of iron and iron nitride microtubes obtained from biogenic iron oxide material were successfully achieved using H_2/N_2 and NH_3 as reductant streams. SEM images indicate that the tubular structure is preserved during the transformation. The formation of iron nitride occurred under ammonia at temperatures higher than 450 °C and the maximum nitrogen content into the solid was observed in the range from 500 to 550 °C. However, nitrogen was not incorporated into the structure when N_2/H_2 was used as feed, and only reduced iron microtubes were observed at temperatures above 400 °C. From the experimental conditions, 500 °C is a suitable temperature for the preparation of reduced and nitrated microtubes from biogenic iron oxide under N_2/H_2 and ammonia, respectively.

Acknowledgements

The authors thank Mr. Gangi Reddy Ubarra for CHN analysis, and James and Christopher Hargreaves for sampling of the iron ochre. In addition, JLR thanks CONACyT for the financial support received during his sabbatical period at the University of Glasgow, Scotland, UK.

The authors confirm that they have no conflict of interest in relation to this study.

References

- [1]. Rentz J (2010) Phosphorus removal potential using biogenic iron oxides, WERF, USA, 2010.
- [2]. Ferris FG, Hallberg RO, Lyvén B, Pedersen K (2000) Retention of strontium, cesium, lead and uranium by bacterial iron oxides from a subterranean environment. *Appl Geochem* 15: 1035-1042.
- [3]. Hargreaves JSJ, Alharthi AI (2016) Biogenic and bio-structured inorganic materials in heterogeneous catalysis: a brief overview. *J Chem Technol Biotechnol* 91: 296–303.
- [4]. Alharthi AI, Blackley RA, Flowers TH, Hargreaves JSJ, Pulford ID, Wigzell J, Zhou W (2014) Iron ochre-a pre-catalyst for the cracking of methane. *J Chem Technol Biotechnol* 89: 1317–1323.
- [5]. Hashimoto H, Itadani A, Kudoh T, Kuroda Y, Seno M, Kusano Y, Ikeda Y, Nakanishi M, Fujii T, Takada J (2013) Acidic Amorphous Silica Prepared from Iron Oxide of Bacterial Origin. *Appl Mater Interfaces* 5: 518–523.
- [6]. Mandai K, Korenaga T, Ema T, Sakai T, Furutani M, Hashimoto H, Takada J (2012) Biogenous iron oxide-immobilized palladium catalyst for the solvent-free Suzuki–Miyaura coupling reaction. *Tetrahedron Lett* 53:329–332.
- [7]. Shopska M, Paneva D, Kadinov G, Todorova S, Fabián M, Yordanova I, Cherkezova-Zheleva Z, Mitov I (2016) Composition and catalytic behavior in CO oxidation of biogenic iron-containing materials. *React Kinet Mech Cat* 118:179–198.
- [8]. Shopska MG, Kadinov GB, Briančin J, Yordanova ID, Kolev HG, Fabián M (2015) Preparation of Fe-Pd/Al-Si-O catalyst using biogenic iron of cultivated *Leptothrix* genus bacteria. *Bulg Chem Commun* Special issue C 47:79–86.
- [9]. Ema T, Miyazaki Y, Kozuki I, Sakai T, Hashimoto H, Takada J (2011) Highly active lipase immobilized on biogenous iron oxide via an organic bridging group: the dramatic effect of the immobilization support on enzymatic function. *Green Chem* 13:3187-3195.
- [10]. Ema T, Miyazaki Y, Taniguchi T, Takada J (2013) Robust porphyrin catalysts immobilized on biogenous iron oxide for the repetitive conversions of epoxides and CO_2 into cyclic carbonates. *Green Chem* 15: 2485–2492.
- [11]. Shopska MG, Cherkezova-Zheleva ZP, Paneva DG, Petkova V, Kadinov GB, Mitov IG (2014) Treatment of Biogenic Iron-Containing Materials. *Croat Chem Acta* 87 (2): 161–170.

- [12] Jozwiak WK, Kaczmarek E, Maniecki TP, Ignaczak W, Maniukiewicz W (2007) Reduction behavior of iron oxides in hydrogen and carbon monoxide atmospheres. *Appl Catal A: Gen* 326:17–27.
- [13] Volpe L, Boudart M (1985) Compounds of molybdenum and tungsten with high specific surface area: I. Nitrides. *J Solid State Chem* 59: 332-347.
- [14] Hashimoto H, Fujii T, Kohara S, Nakanishi K, Yogi Ch, Peterlik H, Nakanishi M, Takada J (2015) Structural transformations of heat-treated bacterial iron oxide. *Mater Chem Phys* 155:67-75.
- [15]. Darken L, Gurry R (1953) *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953, p. 374.
- [16]. Nishimaki K, Ohmae S, Yamamoto TA, Katsura M (1999) Formation of iron-nitride by reaction of iron nanoparticles with a stream of ammonia. *Nanostruct Mater* 12: 527-530.