



## Hydrocarbon oxidation by homogeneous and heterogeneous non-heme iron (III) catalysts with H<sub>2</sub>O<sub>2</sub>

G. Bilis<sup>a</sup>, K.C. Christoforidis<sup>b</sup>, Y. Deligiannakis<sup>b</sup>, M. Louloudi<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Ioannina, Department of Chemistry, 45110 Ioannina, Greece

<sup>b</sup> University of Ioannina, Department of Environmental and Natural Resources Management, Laboratory of Physical Chemistry, Pyllinis 9, 30100 Agrinio, Greece

### ARTICLE INFO

#### Article history:

Available online 11 May 2010

#### Keywords:

Non-heme iron  
Biomimetic catalysis  
Hydrocarbon oxidation  
H<sub>2</sub>O<sub>2</sub>  
Fe–OOH  
Low-spin Fe

### ABSTRACT

Homogeneous (LFe<sup>III</sup>) and heterogeneous (LFe<sup>III</sup>.SiO<sub>2</sub>) [L = 3-{2-[2-(3-hydroxy-1,3-diphenyl-allylideneamino)-ethylamino]-ethylimino}-1,3-diphenyl-propen-1-ol] catalysts have been synthesized and evaluated catalytically. In CH<sub>3</sub>CN, both the homogeneous and heterogeneous catalysts were efficient in alkene oxidations. Cyclohexane oxidation provides total yield of 12.1% and 7.3% with an alcohol/ketone (A/K) ratio of 1.75 and 1.60 by the LFe<sup>III</sup> and the LFe<sup>III</sup>.SiO<sub>2</sub> catalysts respectively. UV–vis kinetic data suggest formation of LFe<sup>III</sup>–OOH species. EPR data show that in the presence of CH<sub>3</sub>CN, low-spin Fe<sup>III</sup> (S = 1/2) centers are formed, which are responsible for the catalytic activity. The heterogeneous LFe.SiO<sub>2</sub> catalyst, tested up to 5 re-uses, shows a total yield loss ~4% per use, providing the same distribution of oxidation products.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

The development of new iron catalysts for hydrocarbon oxidations is attracting synthetic chemists intending to explore new industrial approaches. Nature has evolved iron-enzymes, like non-heme iron oxygenases, capable to carry out hydrocarbon oxidations with high selectivity, under mild conditions. For example, methane monooxygenase [1–3] selectively oxidizes methane to methanol, Rieske dioxygenases [4,5] are capable of stereospecific dihydroxylation of arenes. The antitumor drug iron-bleomycin – a metallo-glycopeptide – causes oxidative DNA cleavage [6,7] and also oxidizes a wide variety of organic substrates [6,8]. Thus, the synthesis of low molecular weight metal complexes aiming to mimic key – structural and – functional properties of natural enzymes is a topic of considerable interest. Of particular, demand is to achieve catalytic efficiency using green oxidants e.g. like H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> [7,9–13]. In this context, stereoselective hydroxylation, epoxidation and *cis*-dihydroxylation by synthetic biomimetic catalysts have been reported [14–22].

In several bioinspired iron-based oxidation catalysts Fe-peroxo species have been invoked to be formed during the catalytic reaction [23,24]. More particularly, a Fe<sup>III</sup>–OOH intermediate has been suggested as key-specie in oxidation reactions of several biomimetic non-heme iron complexes [9]. The formation of the

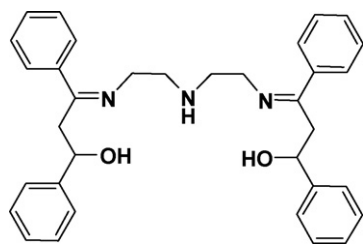
Fe<sup>III</sup>–OOH intermediate is a result of H<sub>2</sub>O<sub>2</sub> deprotonation and subsequent ligation to the Fe<sup>III</sup> center. This Fe<sup>III</sup>–OOH species is the precursor for a high-valent Fe-oxo species, which is responsible for substrate oxidation [2]. Three main pathways can be considered for the cleavage of the O–O bond [25]. (a) Homolytic cleavage leads to a Fe<sup>IV</sup>=O species plus a short-lived highly reactive •OH radical, which is immediately transferred to the substrate [25]. (b) Heterolytic cleavage of the O–O bond generates a Fe<sup>V</sup>=O (analogous to heme-peroxidase) [26] and a OH<sup>–</sup> species. (c) Finally, the Fe<sup>III</sup>–OOH intermediate itself could be involved in substrate oxidation providing an oxidant with moderate reactivity and higher selectivity [27,28].

The heterogenization of catalysts, in contemporary environmentally conscious days, provides important ‘green benefits’ e.g. when solvent and catalyst losses during separation lead to unacceptable waste levels [29]. Thus, replacement of a homogeneous catalyst by an active heterogeneous one changes the synthetic process towards a more desirable and clean one. This provides advantages e.g. easy-handling, easy product separation, catalyst recovery and waste minimization [30]. However, very few literature reports are available on active heterogeneous non-heme iron catalysts functioning with H<sub>2</sub>O<sub>2</sub> [31,32].

In the present work (a) we report the synthesis and catalytic evaluation of (i) a homogeneous LFe<sup>III</sup>Cl and (ii) the heterogeneous LFe<sup>III</sup>.SiO<sub>2</sub> catalyst. L stands for 3-{2-[2-(3-hydroxy-1,3-diphenyl-allylideneamino)-ethylamino]-ethylimino}-1,3-diphenyl-propen-1-ol (Scheme 1). Catalytic oxidations were evaluated using H<sub>2</sub>O<sub>2</sub>. (b) The stability of the catalysts has been also studied. Significant recyclability was found

\* Corresponding author.

E-mail addresses: [ideligia@cc.uoi.gr](mailto:ideligia@cc.uoi.gr) (Y. Deligiannakis), [mlouloud@uoi.gr](mailto:mlouloud@uoi.gr) (M. Louloudi).



**Scheme 1.** The ligand [3-{2-[2-(3-hydroxy-1,3-diphenyl-allylideneamino)-ethylamino]-ethylimino}-1,3-diphenyl-propen-1-ol] (**L**) used herein to form the  $\text{LFe}^{\text{III}}$  catalysts for hydrocarbon oxidation with  $\text{H}_2\text{O}_2$ .

for the heterogeneous  $\text{LFe}^{\text{III}}\cdot\text{SiO}_2$  catalyst. (c) UV–vis kinetic data suggest formation of  $\text{LFe}^{\text{III}}\text{-OOH}$  species and EPR data show that in the presence of  $\text{CH}_3\text{CN}$ , low-spin  $\text{Fe}^{\text{III}}$  ( $S=1/2$ ) centers are formed, which are responsible for the catalytic activity. The synthesis and characterization of the ligand **L** has been reported in our recent reports [33,34] (Scheme 1).

## 2. Experimental

All substrates were purchased from Aldrich, in their highest commercial purity, stored at  $5^\circ\text{C}$  and purified by passage through a column of basic alumina prior to use. Thirty percent aqueous solution of hydrogen peroxide was used. Infrared spectra were recorded on a spectrum GX PerkinElmer FT-IR System. UV–vis spectra were recorded using a UV/VIS/NIR JASCO spectrophotometer and a PerkinElmer Lambda 35 with a diffuse reflectance setup. Fe quantitation was done by Flame Atomic Absorption Spectroscopy (FAAS) on a PerkinElmer AAS-700 spectrometer. Mössbauer spectra were recorded with a constant acceleration spectrometer using a  $^{57}\text{Co}(\text{Rh})$  source at room temperature and a variable temperature. X-Band Electron Paramagnetic Resonance (EPR) spectra were recorded using a Bruker ER200D spectrometer at liquid  $\text{N}_2$  temperatures, equipped with an Agilent 5310A frequency counter running under a home-made software based on LabView described earlier [35]. Mass spectra were measured on an Agilent 1100 Series LC-MSD-Trap-SL spectrometer and solution. GC analysis was performed using an 8000 Fisons chromatograph with a flame ionization detector and a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer.

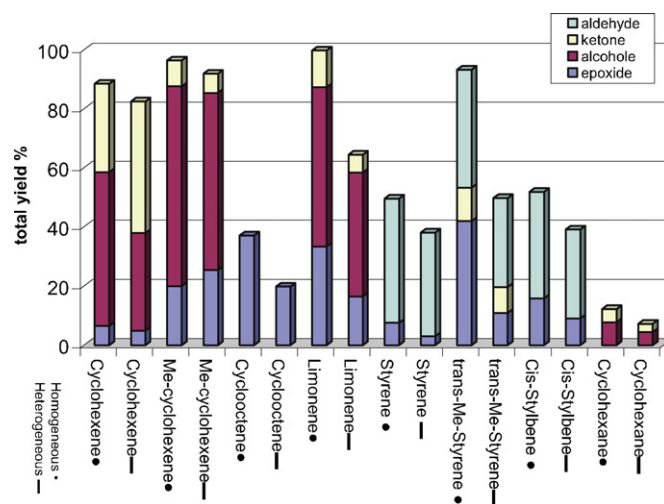
Details about catalyst's preparation and characterization, catalytic experiments, UV–vis and EPR sample preparation are given in Supporting Information.

## 3. Results and discussion

### 3.1. Hydrocarbon oxidation by the homogeneous and heterogeneous $\text{LFe}^{\text{III}}$ catalysts

The catalytic properties of the homogeneous  $\text{LFeCl}$  and heterogeneous  $\text{LFe}\cdot\text{SiO}_2$  catalysts have been evaluated for hydrocarbon oxidation with  $\text{H}_2\text{O}_2$ . The oxidation reactions were carried out at room temperature under Ar atmosphere. When the catalytic experiments took place under air,  $\text{O}_2$  affected both yield and selectivity of the oxidation products. Thus, in the data shown herein all the catalytic reactions were studied under strict inert Ar atmosphere. The catalytic data are summarized in Table 1, and Fig. 1 provides a histogram of them.

Based on Table 1, both the homogeneous and heterogeneous catalysts were efficient in alkene oxidations providing significant yields. More specifically, cyclohexene and limonene oxidation catalyzed by the  $\text{LFeCl}$  provided oxidation products with a combined



**Fig. 1.** Distribution of oxidation products catalyzed by  $\text{LFeCl}$  and  $\text{LFe}\cdot\text{SiO}_2$  in  $\text{CH}_3\text{CN}$  in the presence of  $\text{H}_2\text{O}_2$ . See Table 1 for further details.

yield of 88.5% and 99.8% respectively, while the same reactions catalyzed by the  $\text{LFe}\cdot\text{SiO}_2$  gave combined yields of 82.5% and 64.5%. Cyclohexene undergoes mainly allylic oxidation forming 2-cyclohexene-1-ol and 2-cyclohexene-1-one. However cyclohexene epoxidation was also observed, with low epoxide yields. The major products detected from limonene oxidation were (i) two epoxides (*cis* and *trans*) originating from epoxidation of the electron-rich double bond in 1,2-position, (ii) alcohols derived from hydroxylation of the double bond in 1- and 2-position and from hydroxylation in 6-position close to 1,2-double bond. Oxidation products from the more accessible, but less electron-rich, double bond at 8,9-position were not observed. Additionally, considerable amounts of the corresponding ketone at 6-position were also formed (see details in Table 1). Methyl-substituted alkenes were more reactive, in both epoxidation and allylic oxidation. Thus, in the case of methylcyclohexene, the detected oxidation products were *cis*-epoxide, 1-methyl-2-cyclohexen-1-ol, 3-methyl-2-cyclohexen-1-ol and 3-methyl-2-cyclohexen-1-one. The total yield of methylcyclohexene oxidation products was 96.4% and 91.9% by  $\text{LFeCl}$  and  $\text{LFe}\cdot\text{SiO}_2$  respectively. *Cis*-cyclooctene as substrate afforded a single-product reaction e.g. giving only the *cis*-cyclooctene epoxide with 37.0% and 19.8% yield catalyzed by  $\text{LFeCl}$  and  $\text{LFe}\cdot\text{SiO}_2$  respectively (Fig. 1). In the oxidation of *cis*-stilbene, the major product was benzaldehyde as oxidative cleavage product (36.0% and 30.0% by  $\text{LFeCl}$  and  $\text{LFe}\cdot\text{SiO}_2$  respectively). Considerable amounts of *cis*-stilbene epoxide (15.8% in homogeneous and 9.0% in heterogeneous medium) have been also detected. Styrene oxidation provided also benzaldehyde as major product deriving from oxidative cleavage of the exo-cyclic double bond. However, epoxide and phenyl acetaldehyde have been also formed e.g. by direct oxidation of the same double bond. Overall, styrene was oxidized by  $\text{LFeCl}$  and  $\text{LFe}\cdot\text{SiO}_2$  with total oxidation yields of 49.5% and 38.0% respectively. The methyl-substituted styrene, *trans*- $\beta$ -methyl styrene is more reactive providing total oxidation yields of 93.2% and 49.7% by  $\text{LFeCl}$  and  $\text{LFe}\cdot\text{SiO}_2$  respectively. The identified products were *trans*-epoxide, methyl-benzyl-ketone and benzaldehyde as oxidative cleavage adduct.

Finally, cyclohexane oxidation gave cyclohexanol and cyclohexanone with combined yields of 12.2% and 7.2% and an alcohol/ketone (A/K) ratio of 1.75 and 1.60 for the  $\text{LFe}^{\text{III}}\text{Cl}$  and the  $\text{LFe}^{\text{III}}\cdot\text{SiO}_2$  catalyst respectively. The A/K ratio in cyclohexane can be used as a criterion for the presence and lifetime of free alkyl radical intermediates [24] as follows. (i) When A/K = 1, it assumes that the alkyl radicals are long-lived with a strong tendency to interact

Download English Version:

<https://daneshyari.com/en/article/56203>

Download Persian Version:

<https://daneshyari.com/article/56203>

[Daneshyari.com](https://daneshyari.com)