



Synthesis, characterization and activity of homogeneous and heterogeneous (SiO₂, NaY, MCM-41) iron(III) catalysts on cyclohexane and cyclohexene oxidation

Paula M.A. Machado^a, Leonardo M. Lube^{a,b}, Marcione D.E. Tiradentes^a,
Christiane Fernandes^a, Clícia A. Gomes^a, Alexandre M. Stumbo^a, Rosane A.S. San Gil^c,
Lorenzo C. Visentin^d, Dalber R. Sanchez^e, Vera L.A. Frescura^f, Jesse S.A. Silva^f,
Adolfo Horn Jr.^{a,*}

^a Universidade Estadual do Norte Fluminense Darcy Ribeiro, Laboratório de Ciências Químicas, Campos dos Goytacazes, RJ 28013-602, Brazil

^b Instituto Federal Fluminense, Campus Centro, Campos dos Goytacazes, RJ 28013-602, Brazil

^c Universidade Federal do Rio de Janeiro, Instituto de Química, Laboratório de RMN de Sólidos, Rio de Janeiro, RJ 21941-901, Brazil

^d R&D NanoBusiness e-Diffraction Pharma, Rio de Janeiro, RJ 22451-900, Brazil

^e Universidade Federal Fluminense, Instituto de Física, Campus da Praia Vermelha, Niterói, RJ 24210-346, Brazil

^f Universidade Federal de Santa Catarina, Departamento de Química, Florianópolis, SC 88040-900, Brazil

ARTICLE INFO

Article history:

Received 11 June 2015

Received in revised form 31 August 2015

Accepted 23 September 2015

Available online 30 September 2015

Keywords:

Cyclohexane oxidation

Cyclohexene oxidation

Grafting

Heterogeneous catalysis

Homogeneous catalysis

ABSTRACT

This work deals with the synthesis and characterization of two homogeneous and three heterogeneous iron(III) catalysts, which were evaluated in the oxidation of cyclohexane and cyclohexene, using H₂O₂ as oxidant. The homogeneous catalyst [Fe₂(BPA)₂(μ-OCH₃)₂(Cl)₂], (1), where BPA is the deprotonated form of N-(2-hydroxybenzyl)-N-(pyridin-2-ylmethyl) amine, is a dinuclear iron(III) compound, as determined by X-ray diffraction studies. Compound [Fe^{III}(HBPC/NOL)(Cl)₂], (2), where HBPC/NOL is N-(2-hydroxybenzyl)-N-(2-pyridylmethyl)(3-chloro)(2-hydroxy) propylamine, is a mononuclear iron(III) compound. The reaction of the ligand HBPA with the 3-glycidoxypropyltrimethoxysilane molecule followed by the reaction with different inorganic matrices (silica-gel, NaY zeolite, MCM-41) resulted in the organo functionalized solids SiL, NaYL and MCM-41L, respectively. These materials were reacted with iron(III) salt, affording the heterogeneous catalysts SiLFe, NaYLFe and MCM-41LFe, respectively. They were characterized by elemental analyses, HR-CS AAS, solid state MAS NMR (²⁹Si, ¹³C), IR, UV–vis, TGA, Mossbauer, and textural analyses. The major product formed in all the oxidation reactions was the hydroperoxide derivative. When cyclohexane was the substrate, the homogeneous catalysts were more efficient than the heterogeneous ones. In contrast, the heterogeneous systems showed better results with cyclohexene than with cyclohexane, reaching about 30% in the presence of NaYLFe.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Selective oxidation of unsaturated hydrocarbons is a challenging reaction due to the similarity in the electronegativity of the carbon and hydrogen atoms [1]. In this context, the development of catalysts that may operate at low temperature and pressure for the transformation of relatively cheap and available substrates into valuable functionalized products has attracted the attention from both academy and industry [2]. For example, the production

of cyclohexanone/cyclohexanol, phenol and methanol from cyclohexane, benzene and methane, respectively, are among the top 10 challenges of the modern chemistry [3].

Concerning alkanes, cyclohexane oxidation is particularly interesting in nylon 6 and nylon 6,6 polymers manufacturing, since the oxidation products, cyclohexanol and cyclohexanone (KA oil), are the precursors of adipic acid and caprolactam, obtained by subsequent oxidation using nitric acid [4]. Furthermore, cyclohexanol and cyclohexanone are applied in the production of detergent emulsions, plasticizers, herbicides, insecticides and pharmaceuticals [5].

Currently, the industrial oxidation of cyclohexane employs homogeneous cobalt catalyst and molecular oxygen at a tempera-

* Corresponding author.

E-mail address: adolfo@uenf.br (A. Horn Jr.).

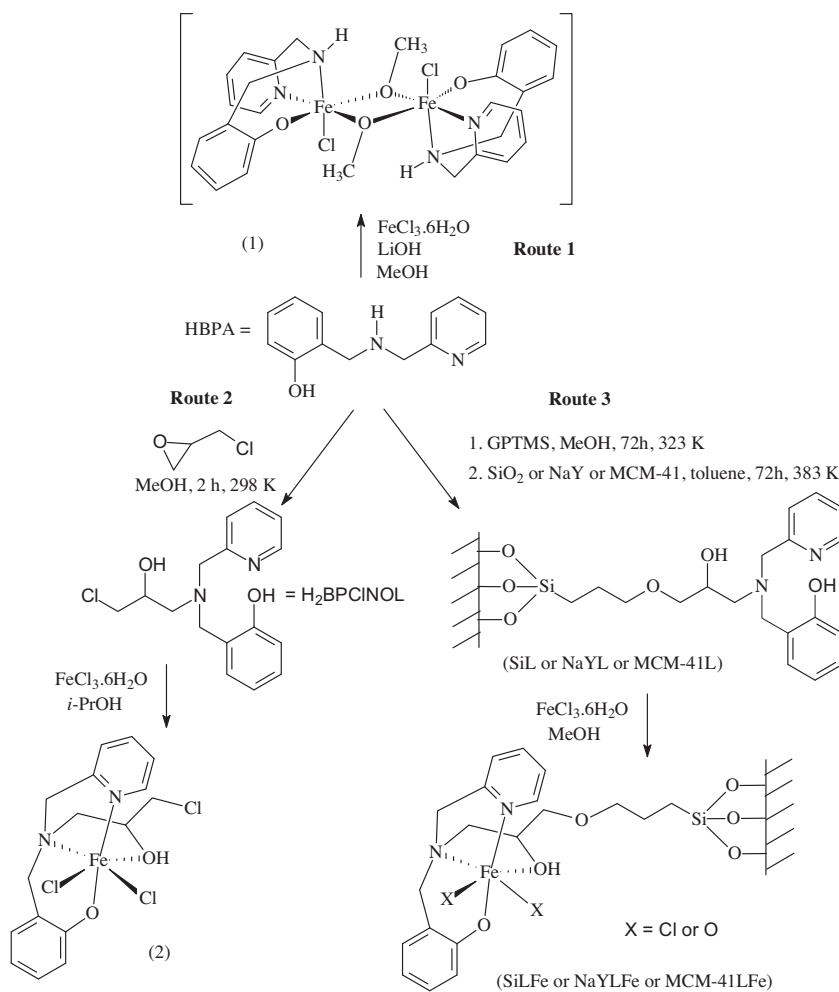


Fig. 1. Scheme of syntheses for the catalysts (1) (Route 1), (2) (Route 2) and SiLFe, NaYLFe or MCM-41Fe (Route 3).

ture between 423 and 433 K and pressure about 0.9 MPa [6]. Despite these drastic conditions, the process obtains about 4% yield and selectivity around 78% for cyclohexanol [1]. This reveals that there is room for the development of more efficient and low energy catalytic processes.

Concerning alkenes, their oxidation reaction is also of relevance because it yields a lot of applicable products like alcohols, ketones, aldehydes, acids and epoxides, which are largely used in food, chemical and pharmaceutical industries [7].

There are different approaches in the literature devoted to the development of catalysts aiming hydrocarbon oxidation, including both homogeneous and heterogeneous processes. Some of them are inspired in biological systems, like cytochrome P-450 and methanemooxygenase enzymes [8–11]. These iron metalloenzymes are oxygenases, able to catalyze the stereospecific oxidation of hydrocarbons under mild conditions, using electron transfer reactions and oxygen transport [12]. These oxygenases generally use molecular oxygen as oxidant to introduce one or two oxygen atoms into their substrates [13]. Concerning cytochrome P450, it is a family of heme protein that can catalyze oxidation reactions like hydroxylation and epoxidation of numerous alkane and alkene substrates [14]. On the other hand, iron methanemooxygenase is a non heme enzyme which converts methane to methanol, into methanotrophic bacteria metabolism [15,16]. Other oxygenases also can oxidize alkenes like toluene ortho-monooxygenase, that convert substrates like toluene, naphthalene and trichloroethy-

lene [13], and Rieske dioxygenases, a class of enzymes able to cis-hydroxylation of aromatic hydrocarbons [17].

The biotransformation, under mild conditions, by these enzymes is selective and efficient. This has called attention to the development of bioinspired catalysts that try to reproduce the active center of these enzymes and solve the oxidation mechanisms, as well [18]. However these enzymes have a limited application in industries, since their isolation and purification are very expensive, there are difficulties in stabilizing the biocatalyst in the reaction medium, problems with product separation, recovery and recycling [19].

Trying to overcome this drawback, iron complexes containing N, O, S donor ligands have been used as bio-inspired catalysts for hydrocarbon oxidation, since similar donor groups are present in the active site of oxidases [20–26]. These systems are characterized by working at room temperature and in the presence of oxidant agents such as peroxides or iodossilbenzene.

Due to the satisfactory results obtained previously with the bioinspired homogeneous catalyst $[\text{Fe}^{\text{III}}(\text{HBPCINOL})(\text{Cl})_2]$ (Fig. 1, compound (2)) in the cyclohexane oxidation [27], we decided to evaluate if the similar, but simpler, compound $[\text{Fe}_2(\text{BPA})_2(\mu\text{-OCH}_3)_2(\text{Cl})_2]$ would be more effective in the oxidation of cyclohexane and cyclohexene than the former one. Furthermore, the ligand H₂BPCINOL was immobilized in silica, NaY-zeolite and MCM-41 matrices, resulting, after reacting with iron(III), in the heterogenized versions of the catalyst $[\text{Fe}^{\text{III}}(\text{HBPCINOL})(\text{Cl})_2]$,

Download English Version:

<https://daneshyari.com/en/article/39173>

Download Persian Version:

<https://daneshyari.com/article/39173>

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