Article

New Trendy Magnetic C-Scorpionate Iron Catalyst and Its Performance towards Cyclohexane Oxidation

Ana P. C. Ribeiro [1,*] , Inês A. S. Matias [1] , Elisabete C. B. A. Alegria [1,2] , Ana M. Ferraria [3], Ana M. Botelho do Rego [3], Armando J. L. Pombeiro [1] and Luísa M. D. R. S. Martins [1,*]

[1] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; ines.matias@tecnico.ulisboa.pt (I.A.S.M.); ebastos@deq.isel.ipl.pt (E.C.B.A.A.); pombeiro@tecnico.ulisboa.pt (A.J.L.P.)

[2] Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal

[3] Centro de Química-Física Molecular and Institute of Nanoscience and Nanotechnology, DEQ, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; ana.ferraria@tecnico.ulisboa.pt (A.M.F.); amrego@tecnico.ulisboa.pt (A.M.B.d.R.)

* Correspondence: apribeiro@tecnico.ulisboa.pt (A.P.C.R.); luisamargaridamartins@tecnico.ulisboa.pt (L.M.D.R.S.M.); Tel.: +351-218419264 (L.M.D.R.S.M.)

Abstract: For the first time, a magnetic C-scorpionate catalyst was prepared from the iron(II) complex [FeCl$_2${κ^3-HC(pz)$_3$}] (pz = pyrazol-1-yl) and ferrite, using the sustainable mechanochemical synthetic procedure. Its catalytic activity for the cyclohexane oxidation with *tert*-butyl hydroperoxide (TBHP) was evaluated in different conditions, namely under microwave irradiation and under the effect of an external magnetic field. The use of such magnetic conditions significantly shifted the catalyst alcohol/ketone selectivity, thus revealing a promising, easy new protocol for tuning selectivity in important catalytic processes.

1. Introduction

The recovery and reuse of catalysts is still a challenge in the development of sustainable chemical processes. Loading the catalyst onto a magnetic material has recently emerged as a new synthetic procedure addressing this problem with significance in green chemistry [1–6].

The catalyst preparation is itself a very important issue to consider in the design of sustainable processes. In this regard, mechanochemistry, particularly dry ball milling synthesis, is appealing as it eliminates the need for solvents and drastically reduces the energy input [7–9].

Among the current relevant industrial oxidative processes, the well-established homogeneous cyclohexane oxidation, as part of the large scale (~4 million ton/year) Nylon 6 production, presents several drawbacks related to the catalyst selectivity (which is only able to generate 5–12% yields to assure a selectivity of ca. 80–85% [10]) and requires urgent improvement [10–12].

Within the known homogeneous catalysts for alkanes oxidation, metallic complexes with C-scorpionate tris(pyrazol-1-yl)methane ligands have gained significant importance in the last years [13–17]. The bio-inspired tris(pyrazol-1-yl)methane iron(II) complex [FeCl$_2${κ^3-HC(pz)$_3$}], which was previously proved to act as an efficient catalyst in C–H activation reactions [13–20], was also chosen due to its easy (one-step) synthesis in water at room temperature [18].

Therefore, in pursuit of our interest in the sustainable oxidation of alkanes, the main objectives of the present study consisted of the development of an improved catalytic process for the oxidation of cyclohexane by taking advantage of the unique properties of the magnetized C-scorpionate iron(II)

catalyst (e.g., its recyclability and reuse by easy magnetic separation) prepared by an eco-friendly route. Moreover, we also aimed at an evaluation of the effect of an external magnetic field on the catalytic performance of our new magnetic material.

To our knowledge, this is the first time that the successful preparation of a magnetic scorpionate catalyst and the use of an external magnetic field for tuning the oxidation of alkanes has been reported.

2. Results and Discussion

The iron(II) complex [$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$] (**1**, pz = pyrazol-1-yl) was synthesized according to a reported procedure [18] and characterized by spectroscopic and analytic techniques.

The new magnetic iron catalyst (**2**) was prepared by dry milling treatment of [$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$] and ferrite (1:1 mass ratio) at room temperature (see Section 3.1).

Three samples were analysed by XPS: The C-scorpionate iron complex ([$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$], **1**); the ferrite sample (Fe_3O_4); and the mixture [$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$] + Fe_3O_4 (1:1, wt. %, **2**). Figure 1 shows the photoelectron C 1s and Fe 2p XPS regions and the valence band of the mixture compared with the sum of [$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$] and Fe_3O_4 valence bands.

Figure 1. *Cont.*
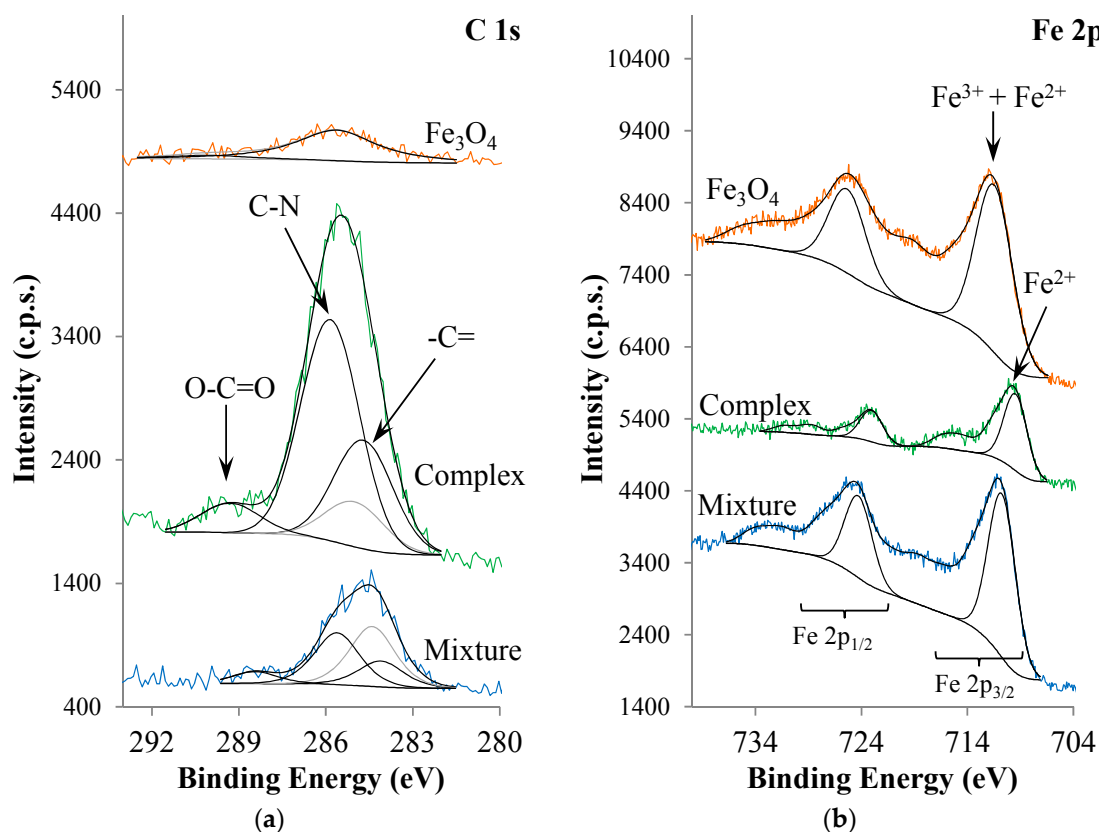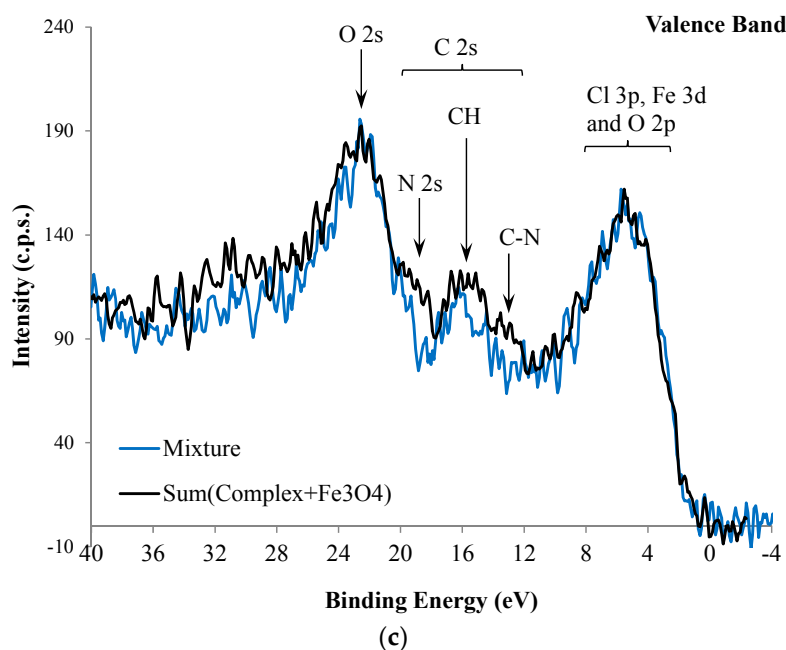
Figure 1. XPS regions (**a**) C 1s and (**b**) Fe 2p of (from top to bottom): Fe_3O_4, $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$ (**1**) and their mixture (**2**). (**c**) Comparison of the mixture valence band with the sum of $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$ and Fe_3O_4 valence bands.

The iron(II) complex C 1s region (Figure 1a) was fitted with two main peaks, assigned to sp^2 carbon atoms (–C=) and carbon singly bound to nitrogen (C–N), plus two extra peaks from some aliphatic carbon (grey curve) and one peak centered at higher binding energies, characteristic of carbon atoms in very electronegative neighborhoods such as carboxyl and/or carboxylate groups. After mixing with Fe_3O_4, C 1s fitting is qualitatively very similar to that of the complex $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$, although the relative amount of aliphatic carbon has increased. Such carbonaceous contamination mainly results from Fe_3O_4, as attested by the carbon detected in the ferrite sample. Fe 2p regions (Figure 1b) were fitted with several doublets, but only the most intense are shown. Centered at a lower binding energy, the complex **1** has a component, Fe $2p_{3/2}$, centered at 709.4 ± 0.2 eV, which is typical of Fe^{2+}. As expected, this component binding energy increases in the presence of Fe_3O_4 to 710.7 ± 0.2 eV, attesting that Fe 2p is a sum of Fe^{2+} and Fe^{3+} ions [21]. Fe $2p_{3/2}$ in Fe_3O_4 is centered at 711.5 ± 0.2 eV. Roughly between 715 and 723 eV and above 729 eV, multiplet structures arising from spin-spin coupling (between unpaired core electron and the unpaired electrons in the outer shell) are detected.

XPS analysis shows that the as-synthesised iron(II) complex $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$ has the expected Fe/N ratio (0.17, Table 1); however, the atomic ratio N/Cl = 4.0 (against 3.0 for the anticipated stoichiometry) is compatible with some chloride loss or chloride atoms shared between complexes. In fact, from the quantitative analysis of C 1s fitted peaks, the experimental C_{sp}^2/C-N atomic ratio (computed from the areas of the main peaks identified in Figure 1a) is close to the one predicted for the as-synthesized $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$ (~1.2), which means that the detected O–C=O groups must be from carboxylated iron, which could promote some dimerization.

When mixed with Fe_3O_4, complex **1** seems to lose nitrogen atoms, as shown by the ratio N/Cl (N and Cl only exist in the organometallic compound) <3.0. Also, the large ratio C/N = 2.7 quantified in the mixture is compatible with nitrogen depletion, although the formation of some carbonaceous contamination after milling cannot be discarded, as attested by C 1s regions of Fe_3O_4 and the mixture (Figure 1a). Moreover, when comparing the mixture valence band (VB) with the sum of individual valence bands ($VB_{Complex} + VB_{Fe3O4}$) (Figure 1c), it is clear that the shoulders detected in the sum spectrum, around 18 eV and 13 eV assigned to N 2s and C–N, respectively, have a lower intensity in the mixture, favouring the nitrogen depletion hypothesis.

Table 1. Experimental XPS atomic ratios and expected ratios for $[FeCl_2\{\kappa^3\text{-HC(pz)}_3\}]$ (**1**), Fe_3O_4 and their (1:1) mixture (**2**).

Atomic Ratios	Expected	Experimental	
	$[FeCl_2\{\kappa^3\text{-HC(pz)}_3\}]$	$[FeCl_2\{\kappa^3\text{-HC(pz)}_3\}]$	$[FeCl_2\{\kappa^3\text{-HC(pz)}_3\}]$ + Fe_3O_4
Fe/N	0.17	0.18	2.4
N/Cl	3.0	4.0	1.7
C/N	1.7	2.2	2.7
	Fe_3O_4		
O/Fe	1.3	-	1.2

In order to evaluate the morphology of the $[FeCl_2\{\kappa^3\text{-HC(pz)}_3\}]$ + Fe_3O_4 (1:1) material (**2**), characterization by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was performed (Figure S1, Supplementary Materials). The mixture exhibits a similar morphology to the $[FeCl_2\{\kappa^3\text{-HC(pz)}_3\}]$ before ball milling. Although the milling speed (510 rpm) is already considered high power ball milling, the duration of the mixing (1 h) was not enough to dramatically decrease the size of the compounds. The mixture of both compounds is observed in both images (Figure S1a,b), confirming that ball milling is an efficient method for performing solvent-free mixtures.

The thermal stability of mixture **2** was evaluated by TGA (Figure S2, Supplementary Materials). The weight loss percentage is insignificant in the temperature range to be used in the catalytic experiments. Moreover, as expected, at the end of the analysis, the mixture maintained its magnetic character.

The magnetic mixture **2** was used as a catalyst for the oxidation of cyclohexane to KA oil [cyclohexanol (A, CyOH) and cyclohexanone (K, CyO)], with TBHP (70% aqueous solution) in the conventional solvent CH_3CN (Scheme 1). Two different protocols were used (i) microwave (MW) assisted and (ii) under the effect of an external magnetic field.
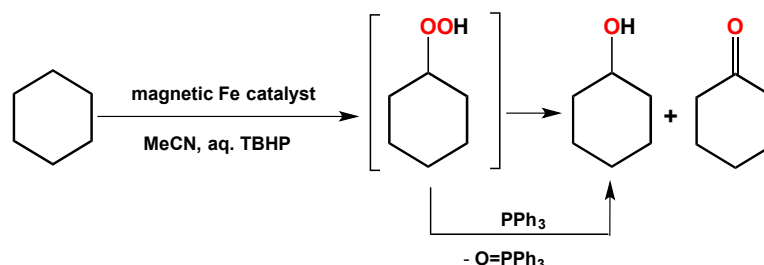
Scheme 1. Oxidation of cyclohexane by TBHP catalyzed by **2**.

(i) Microwave (MW) assisted oxidation of cyclohexane

The performance of the magnetic C-scorpionate catalyst **2** was evaluated in terms of products yield, turnover number (TON) or frequency (TOF, h^{-1}), and selectivity as a function of the reaction time and the presence of a co-catalyst (e.g., pyrazinecarboxylic acid, Hpca) (Table 2).

The best catalytic conditions were found when using **2**, the oxidant *tert*-butyl hydroperoxide (*t*-BuOOH, TBHP, 70% aqueous solution) and the solvent acetonitrile (MeCN), in acidic medium (pyrazine carboxylic acid, Hpca) and under microwave (MW) irradiation at 50 °C during 6 h (Table 2). The use of different acidic additives (entries 5 and 6, Table 2) or of hydrogen peroxide (entry 12, Table 2) instead of TBHP did not improve the catalytic system. Importantly, KA oil (cyclohexanol and cyclohexanone mixture) was the only product detected by GC analysis, revealing the high selectivity of the catalytic oxidative system under the above reaction conditions.

The yield values achieved (30%, entry 3, Table 2) with the magnetic mixture **2** are considerably higher than those provided by the current industrial process (homogeneous cobalt catalyst, dioxygen at 150 °C [10]) and comparable to those previously obtained when **1** was submitted to microwave irradiation (total yield of 33%) in the presence of Hpca [22]. The ferrite (Fe_3O_4) or the $FeCl_2 \cdot 2H_2O$ salt exhibited significantly lower catalytic activity (entries 9 and 14, respectively, Table 2) than mixture **2**, suggesting the favorable involvement of the scorpionate ligands in the metal-assisted steps [13] (Equations (1) and (2)) of this oxidation reaction that led to the radical species (e.g., $^tBuO^\bullet$) able to generate the cyclohexyl radical by H-abstraction.
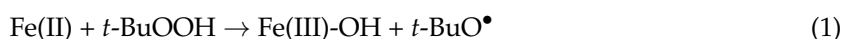
Table 2. Selected data ^{a} for the cyclohexane oxidation to KA oil with aqueous TBHP, catalyzed by the magnetic $[FeCl_2\{HC(pz)_3\}] + Fe_3O_4$ (**2**).

Entry	Time/h	Additive	Yield/% ^{b}			A/K ^{c}	Total TON ^{d}	Total TOF/h^{-1} ^{e}
			CyO (K)	CyOH (A)	Total			
1	1	Hpca	7.3	11.3	18.6	1.5	93	93
2	3	Hpca	9.9	18.9	28.8	1.9	144	48
3	6	Hpca	10.3	19.2	29.5	1.9	147	25
4	3	no additive	3.3	1.5	4.8	0.5	24	8
5	1	HNO$_3$	1.2	2.3	3.5	1.9	17.5	18
6	1	H$_2$SO$_4$	1.8	1.9	3.7	1.1	18.5	19
7	1	TEMPO	1.2	1.7	2.9	1.4	14.5	15
8 ^{f}	3	Hpca	14.7	12.3	27	0.8	135	45
9 ^{g}	3	Hpca	2.9	2	4.9	0.7	24.5	8
10 ^{h}	1	Hpca	5.3	6.2	11.5	1.2	57.5	58
11 ^{i}	1	Hpca	10.3	16.3	26.6	1.6	133	133
12 ^{j}	1	Hpca	4.1	8.3	12.4	2.0	62	62
13 ^{k}	6	Hpca	12.4	20.6	33.0	0.6	165	28
14 ^{l}	6	Hpca	1.6	0.9	2.5	0.6	12.5	2

^{a} Reaction conditions, unless stated otherwise: MeCN (3.0 mL), CyH (5.0 mmol), TBHP (70% aqueous solution, 10.0 mmol), **2** (10 mg), $n_{(additive)} = 4 \times 10^{-2}$ µmol, 50 °C, MW (5 W). ^{b} Based on gas chromatographic (GC) analysis, after treatment with PPh$_3$; total yields in moles of cyclohexanol + cyclohexanone per 100 moles of cyclohexane. ^{c} Ratio between the concentrations of A and K. ^{d} TON = Total turnover number (moles of cyclohexanol + cyclohexanone per mol of catalyst). ^{e} TOF (h^{-1}) = TON/time. ^{f} Without PPh$_3$ treatment. ^{g} With Fe$_3$O$_4$ as catalyst. ^{h} $n_{(additive)} = 1 \times 10^{-2}$ µmol. ^{i} $n_{(additive)} = 8 \times 10^{-2}$ µmol. ^{j} H$_2$O$_2$ (30% aqueous solution, 10.0 mmol). ^{k} With FeCl$_2 \cdot 2H_2O$ as catalyst. ^{l} With FeCl$_2 \cdot 2H_2O$ as catalyst.

Control experiments in the absence of **2**, with *t*-BuOOH, confirm the crucial role of **2** to efficiently catalyse the oxidation of cyclohexane.

Moreover, when in the presence of the known radical trap 2,2,6,6-tetramethylpiperidyl-1-oxyl radical (TEMPO), a marked decrease (85%, compare entries 1 and 7, Table 2) in the products yield was observed, suggesting the involvement of a radical mechanism [23].

$$Fe(II) + t\text{-BuOOH} \rightarrow Fe(III)\text{-OH} + t\text{-BuO}^\bullet \tag{1}$$

$$Fe(III) + t\text{-BuOOH} \rightarrow Fe(II) + t\text{-BuOO}^\bullet + H^+ \tag{2}$$

(ii) Cyclohexane oxidation under the effect of an external magnetic field

The performance of the magnetic C-scorpionate catalyst **2** was also tested using the above reaction conditions but under an external magnetic field [neodymium magnet(s)] at 35 °C, instead of the MW irradiation (Figure 2).

As shown in Table 3, with this new optimized procedure (magnetic **2** under an external magnetic field), 100% selectivity towards cyclohexanol formation is obtained (entries 1–6, Table 3). Only for longer reaction times, the incipient formation of cyclohexanone is detected (entry 3, Table 3). However, the characteristics (e.g., magnetization, strength, or configuration) of the applied magnetic field can significantly influence the alcohol/ketone selectivity (compare entries 3, 7, and 8, Table 3, corresponding

to the different external NdFeB magnetic fields depicted in Figure 2a–c, respectively). Such effects are now the target of our further studies. Nevertheless, the selectivity outcome from the reaction performed under the same conditions except not submitted to an external magnetic field is completely different (entry 9, Table 3), leading to a ca. 1:1 cyclohexanol:cyclohexanone mixture.

(a)

(b)

(c)
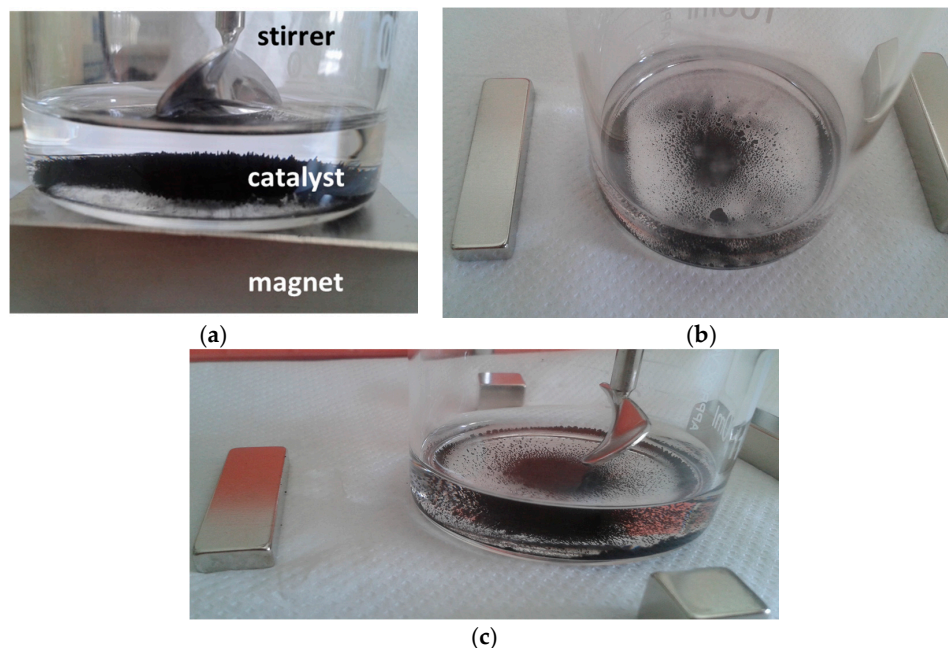
Figure 2. Cyclohexane oxidation reaction performed under different external NdFeB magnetic fields. (**a**) One magnetic block N40 grade; (**b**) Two magnetic blocks N42 grade; (**c**) Two magnetic blocks N42 grade, a magnetic cube N42 grade, and a magnetic cube N48 grade.

Table 3. Selected data [a] for the cyclohexane oxidation with TBHP using [FeCl$_2${HC(pz)$_3$}] + Fe$_3$O$_4$ (**2**) as catalyst, under an external magnetic field.

Entry	Time/h	Additive	Yield/% [b]			Total TON [c]	Total TOF/h^{-1} [d]
			CyO (K)	CyOH (A)	Total		
1 [a]	1	Hpca	0	2.3	2.3	11.5	12
2 [a]	3	Hpca	0	3.3	3.3	16.5	6
3 [a]	6	Hpca	0.6	6.8	7.4	37	6
4 [a]	3	no additive	0	5.7	5.7	28.5	10
5 [a,e]	6	Hpca	0	2	2	10	2
6 [a,f]	3	Hpca	0	1.1	1.1	5.5	2
7 [g]	6	Hpca	2.3	5	7.3	36.5	6
8 [h]	6	Hpca	2.1	4.9	7.0	35.0	6
9 [i]	6	Hpca	3.7	3.2	6.9	34.5	6

[a] Reaction conditions, unless stated otherwise: MeCN (3.0 mL), CyH (5.0 mmol), TBHP 70% aqueous solution (10.0 mmol), **2** (10 mg), $n_{(additive)} = 4 \times 10^{-2}$ µmol, 35 °C, NdFeB magnetic field of Figure 2a. [b] Based on GC analysis, after treatment with PPh$_3$; total yields in moles of cyclohexanol + cyclohexanone per 100 moles of cyclohexane. [c] TON = Turnover number (mol of cyclohexanol + cyclohexanone/mol of catalyst). [d] TOF (h^{-1}) = TON/time (h). [e] H$_2$O$_2$ 30% aqueous solution (10.0 mmol) instead of TBHP. [f] With Fe$_3$O$_4$ as catalyst. [g] With the NdFeB magnetic field of Figure 2b. [h] With the NdFeB magnetic field of Figure 2c. [i] Without an external magnetic field.

Recently, the possibility of tuning the selectivity towards alcohol or ketone formation by choosing the appropriate solvent was previously found [22,24] for **1**: in supercritical CO$_2$ and in the ionic liquids [bmim]X [X = N(CN)$_2$, [BF$_4$], [PF$_6$] or FAP] (bmim = 1-butyl-3-methylimidazolium; FAP = tris(pentafluoroethyl)trifluorophosphate). Such solvent selectivity was also found for the cyclohexane oxidation catalyzed by ferrocene [25] or a Cu(II) complex [26] in some of the above ionic

liquids. However, to date, there is no report concerning the application of an external magnetic field in a procedure for the selective oxidation of cyclohexane.

The use of an external field to tune selectivity is a new concept than can potentially change how the catalysts are perceived, since the orientation of a catalyst is not a usual parameter in the optimization of catalytic oxidative conditions.

Another advantage of our magnetic catalytic system is the easy separation of the catalyst at the end of the reaction [using either method (i) or (ii)] by the easy and convenient application of an external magnetic field, and its recyclability.

The stability of **2** was tested in terms of its re-usability in consecutive cycles (see Section 3.3) for both oxidative methods (microwave-assisted and under an external magnetic field) and is depicted in Figure 3.
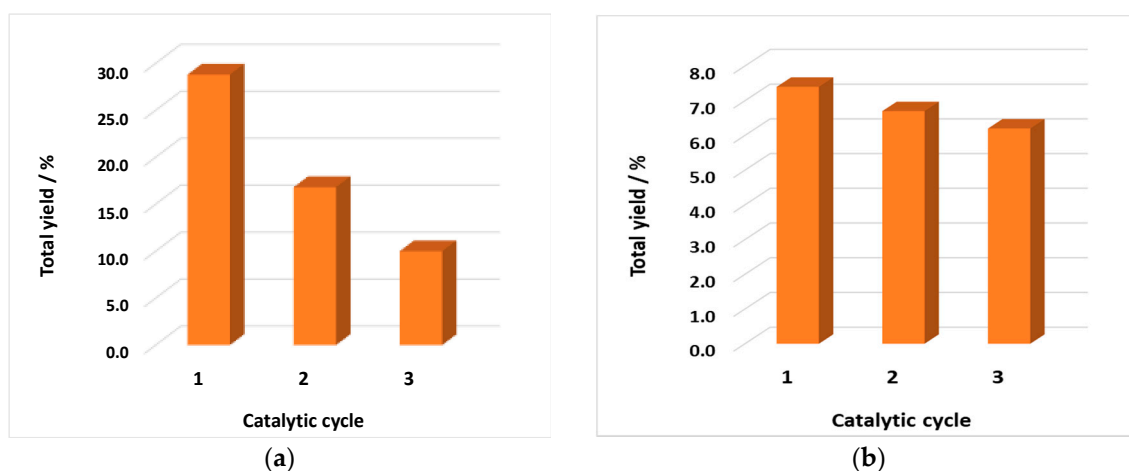
Figure 3. Effect of the magnetic mixture **2** recycling on the products yield of cyclohexane oxidation with TBHP (**a**) reaction conditions: 3 h, 50 °C, MW (5 W); (**b**) reaction conditions: 6 h, 35 °C, external magnetic field.

Under microwave (MW) irradiation at 50 °C during 6 h, the recycling studies showed a loss of 40% in the activity relative to the first run, which is probably due to mixture decomposition under the oxidant conditions used. Under the external magnetic field, similar behavior is observed, but the loss in activity is smaller (17%). The UV/vis analysis of the corresponding supernatant phases (using MW irradiation or a magnetic field) after the first cycle revealed leaching of **2** in both catalytic methods, being more extensive for the first one. This could account for the observed loss of activity in the subsequent recycling cycles (Figure 3).

3. Materials and Methods

All the reagents and solvents were purchased from Sigma-Aldrich (Munich, Germany) and used as received. The scorpionate complex **1** [18] and the magnetic ferrite [27] were synthesized and characterized according to methods described in the literature.

3.1. Experimental Section

TEM measurements were performed on a Transmission Electron Microscope Hitachi 8100 with a ThermoNoran light elements EDX detector and digital image acquisition (Hitachi, Tokyo, Japan). Morphology and distribution of metal composites were characterized using a scanning electron microscope (SEM, EDS) JEOL 7001F with an Oxford light elements EDX detector and EBSD detector (JEOL, Tokyo, Japan).

A dual anode XSAM800 spectrometer was used for X-ray Photoelectron Spectroscopy (XPS) characterization (KRATOS, Manchester, UK). Spectra were obtained using non-monochromatic Al Kα X-radiation (hν = 1486.6 eV) produced with a power of 120 W, in FAT mode, high magnification, pass energy of 20 eV, and at TOA = 45°. Data collection and processing details are described elsewhere [28]. The charge shifts were corrected using the aliphatic carbon binding energy centered at 285 eV as the reference. A fine readjustment of the mixture and ferrite charge shift corrections was performed by matching O 2s and C 2s features. The sensitivity factors were: 0.278 for C 1s, 0.78 for O 1s, 0.891 for Cl 2p, 0.477 for N 1s, and 2.957 for Fe 2p.

The magnet material is NdFeB, Nickel-plated (Ni-Cu-Ni): one magnetic block (Size 50.8 × 50.8 × 25.4 mm; Tolerance +/−0.1 mm) with N40 magnetization and a strength of approx. 100 kg; two magnetic blocks (Size 40.0 × 40.0 × 10.1 mm; Tolerance +/−0.1 mm) N42 magnetization and strength of approx. 15 kg; one cube (Size 10.0 × 10.0 × 10.0 mm; Tolerance +/−0.1 mm) N42 magnetization and a strength of approx. 3.8 kg; and a magnetic cube (Size 12.0 × 12.0 × 12.0 mm; Tolerance +/−0.1 mm) N48 magnetization and strength of approx. 6.3 kg.

The microwave used is an Anton Paar, monowave 300, with a G10 borosilicate glass reactor (Anton Paar GmbH, Graz, Austria).

The UV/vis analyses were performed in a Lambda 25, Perkin Elmer, with quartz cells with a 1 cm path length (PerkinElmer, Inc., Waltham, MA, USA).

3.2. Preparation of the Dispersed Catalyst

During the dry milling treatment, the [FeCl$_2$\{κ^3-HC(pz)$_3$\}] (pz = pyrazol-1-yl) and the magnetic ferrite (ratio 1:1) were mixed mechanically, during 1 h, in a Retsch PM100/200 planetary ball mill, equipped with a 50 mL grinding bowl and 10 stainless steel balls of a 10 mm size. The rotational speed was 450 rpm, with rotational inversions every 5 min. All the mixtures were prepared in the absence of any added solvent (dry milling). After, the produced mixture was left under N$_2$, at 200 °C, for 12 h, to eliminate the possible presence of CO$_2$ and water from the mixture.

3.3. Procedure for the Catalytic Oxidations

The microwave-assisted cyclohexane oxidation using CH$_3$CN as a solvent (up to 5 mL total volume) was performed in a glass reactor (i.e., a Pyrex tube). The catalyst was added to the solvent as a solid in the reaction medium. Cyclohexane (5 mmol) was then introduced, and the reaction started when 70% TBHP aqueous solution as the oxidant (10 mmol) was added in one portion and the tube was sealed. The tube was placed in the microwave reactor and the system was left under stirring and under MW-irradiation (5 W), at 50 °C for 1–6 h. The reaction was stopped after the desired time and 5 mL of diethyl ether was added for the extraction of the organic products.

The reaction mixtures were analyzed by gas chromatography (GC) upon the addition of an excess of triphenylphosphine to reduce cyclohexyl hydroperoxide to cyclohexanol, following a method developed by Shul'pin [29]. Nitromethane (0.05 mL) was used as an internal standard. Chromatographic measurements were performed in a Fisons Instruments GC 8000 series gas chromatograph with a BP20/SGE (30 m × 0.22 mm × 0.25 mm) capillary column (flame ionization detector (FID) detector) and Jasco-Borwin v.1.50 software (Jasco, Tokyo, Japan), using helium as a carrier gas. All products formed were identified and their retention times were confirmed with those of commercially available samples. Helium was used as the carrier gas. Blank experiments in CH$_3$CN were performed and it was confirmed that no cyclohexane oxidation products (or only traces, below 1%) were obtained in the absence of the iron catalyst.

The cyclohexane oxidation under an external magnetic field using CH$_3$CN as the solvent (up to 5 mL total volume) was performed in a common beaker. The catalyst was added to the solvent as a solid in the reaction medium. Cyclohexane (5 mmol) was then introduced, and the reaction started when 70% TBHP aqueous solution as the oxidant (10 mmol) was added in one portion. The beaker was placed in the magnetic field (see Figure 2) and the system was left under mechanical stirring at

room temperature for 1–6 h. The reaction was stopped after the desired time and 5 mL of diethyl ether was added for the extraction of the organic products. The reaction mixtures were analyzed by GC as described above.

3.4. Catalyst Recycling

Catalyst recyclability was investigated, and each new cycle was initiated after the preceding one upon removal of the catalyst with a magnet, washing it with diethyl ether and drying it at 60 °C for 2 h. Then, it was added to the new typical (see above) portions of all other reagents and a new reaction was performed. After the completion of each run, the products were analyzed as previously described in point Section 3.2.

4. Conclusions

In this study, the first magnetic C-scorpionate iron mixture is reported. Moreover, its synthesis was performed by a simple and clean mechanochemical procedure. This study has also initiated exploration of the catalytic properties of the magnetic C-scorpionate iron mixture for alkane oxidations using non-conventional methods: (i) microwave (MW) assisted and (ii) under the effect of an external magnetic field. In procedure (i), notorious catalytic efficiency in the oxidation of cyclohexane to KA oil was found (yields up to ca. 29%), whereas route (ii) exhibited an unusually high selectivity for cyclohexanol. These promising results encourage further extension of the investigation to other alkanes and magnetic catalysts.

Author Contributions: Ana Paula da Costa Ribeiro and Luísa M. D. R. S. Martins conceived and designed the experiments; Inês Andreia Simão Matias prepared the catalysts; Ana Maria Ferraria and Ana M. Botelho do Rego performed the XPS analyses; Ana P. C. Ribeiro, Inês A. S. Matias and Elisabete C. B. A. Alegria performed the catalytic experiments; Ana P. C. Ribeiro and Luísa M. D. R. S. Martins analyzed the data and wrote the paper; Luísa M. D. R. S. Martins and Armando J. L. Pombeiro provided the means needed for the realization of this work; All authors read and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. Lu, A.-H.; Salabas, E.L.; Schüth, F. Magnetic nanoparticles: Synthesis, protection, functionalization, and application. *Angew. Chem. Int. Ed.* **2007**, *46*, 1222–1244. [CrossRef] [PubMed]
2. Shylesh, S.; Schünemann, V.; Thiel, W.R. Magnetically Separable Nanocatalysts: Bridges between Homogeneous and Heterogeneous Catalysis. *Angew. Chem. Int. Ed.* **2010**, *49*, 3428–3459. [CrossRef] [PubMed]
3. Zhu, Y.; Stubbs, L.P.; Ho, F.; Liu, R.; Ship, C.P.; Maguire, J.A.; Hosmane, N.S. Magnetic Nanomixtures: A New Perspective in Catalysis. *ChemCatChem* **2010**, *2*, 365–374. [CrossRef]
4. Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. Magnetically Recoverable Nanocatalysts. *Chem. Rev.* **2011**, *111*, 3036–3075. [CrossRef] [PubMed]
5. Rossi, L.M.; Costa, N.J.S.; Silva, F.P.; Wojcieszak, R. Magnetic nanomaterials in catalysis: Advanced catalysts for magnetic separation and beyond. *Green Chem.* **2014**, *16*, 2906–2933. [CrossRef]
6. Wang, D.; Astruc, D. Fast-Growing Field of Magnetically Recyclable Nanocatalysts. *Chem. Rev.* **2014**, *114*, 6949–6985. [CrossRef] [PubMed]

7.   Baláž, P. *Mechanochemistry in Nanoscience and Minerals Engineering*; Springer: Berlin, Germany, 2008.

8.   Stolle, A.; Ranu, B. (Eds.) *Ball Milling towards Green Synthesis Applications, Projects, Challenges*; Royal Society of Chemistry (RCS): London, UK, 2015.

9.   Ribeiro, A.P.C.; Fontolan, E.; Alegria, E.C.B.A.; Kopylovich, M.N.; Bertani, R.; Pombeiro, A.J.L. The influence of multiwalled carbon nanotubes and graphene oxide additives on the catalytic activity of 3d metal catalysts towards 1-phenylethanol oxidation. *J. Mol. Catal. A Chem.* **2017**, *426*, 557–563. [CrossRef]

10.   Estes, L.L.; Schweizer, M. Fibers, 4 Polyamide Fibers. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, Germany, 2011; Volume 11, pp. 41–49.

11.   Ahmed, J.; Ahuja, S.; Ali, I.; Anderson, C.; Anderson, M.J.; Arai, Y.; Braglia, M.; Babirad, S.; Bag, D.; Bagchi, A.; et al. *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley & Sons: New York, NY, USA, 2014.

12.   Clerici, M.G.; Ricci, M.; Strukul, G. *Metal-Catalysis in Industrial Organic Processes*; Chiusoli, G.P., Maitlis, P.M., Eds.; Royal Society of Chemistry: Cambridge, UK, 2006.

13.   Martins, L.M.D.R.S.; Pombeiro, A.J.L. Tris(pyrazol-1yl)methane metal complexes for catalytic mild oxidative functionalizations of alkanes, alkenes and ketones. *Coord. Chem. Rev.* **2014**, *265*, 74–88. [CrossRef]

14.   Martins, L.M.D.R.S.; Pombeiro, A.J.L. Water-soluble C-scorpionate complexes: Catalytic and biological applications. *Eur. J. Inorg. Chem.* **2016**, *15–16*, 2236–2252. [CrossRef]

15.   Martins, L.M.D.R.S. C-homoscorpionate oxidation catalysts—Electrochemical and catalytic activity. *Catalysts* **2017**, *7*, 12. [CrossRef]

16.   Ribeiro, A.P.C.; Martins, L.M.D.R.S.; Pombeiro, A.J.L. N_2O-free single-pot conversion of cyclohexane to adipic acid catalysed by an iron(II) scorpionate complex. *Green Chem.* **2017**, *19*, 1499–1501. [CrossRef]

17.   Mendes, M.; Ribeiro, A.P.C.; Alegria, E.C.B.A.; Martins, L.M.D.R.S.; Pombeiro, A.J.L. Liquid phase oxidation of xylenes catalyzed by the tripodal C-scorpionate iron(II) complex [FeCl$_2$\{κ^3-HC(pz)$_3$\}]. *Polyhedron* **2017**, *125*, 151–155. [CrossRef]

18.   Silva, T.F.S.; Alegria, E.C.B.A.; Martins, L.M.D.R.S.; Pombeiro, A.J.L. Scorpionate vanadium, iron and copper complexes as selective catalysts for the peroxidative oxidation of cyclohexane under mild conditions. *Adv. Synth. Catal.* **2008**, *350*, 706–716. [CrossRef]

19.   Martins, L.M.D.R.S.; Martins, A.; Alegria, E.C.B.A.; Carvalho, A.P.; Pombeiro, A.J.L. Efficient cyclohexane oxidation with hydrogen peroxide catalysed by a C-scorpionate iron(II) complex immobilized on desilicated MOR zeolite. *Appl. Catal. A Gen.* **2013**, *464–465*, 43–50. [CrossRef]

20.   Martins, L.M.D.R.S.; Peixoto de Almeida, M.; Carabineiro, S.A.C.; Figueiredo, J.L.; Pombeiro, A.J.L. Heterogenisation of a C-scorpionate Fe(II) complex in carbon materials for cyclohexane oxidation with hydrogen peroxide. *ChemCatChem* **2013**, *5*, 3847–3856. [CrossRef]

21.   Naumkin, A.; Kraut-Vass, V.A.; Gaarenstroom, S.W.; Powell, C.J. (Eds.) *NIST X-ray Photoelectron Spectroscopy Database*; Standard Reference Database 20, Measurement Services Division of the National Institute of Standards and Technology (NIST); Material Measurement Laboratory (MML): Gaithersburg, MD, USA, 2012.

22.   Ribeiro, A.P.C.; Martins, L.M.D.R.S.; Kuznetsov, M.L.; Pombeiro, A.J.L. Tuning Cyclohexane Oxidation: Combination of microwave irradiation and ionic liquid with the C-scorpionate [FeCl$_2$(Tpm)] catalyst. *Organometallics* **2017**, *36*, 192–198. [CrossRef]

23.   Kopylovich, M.N.; Mahmudov, K.T.; Silva, M.F.C.G.; Martins, L.M.D.R.S.; Kuznetsov, M.L.; Silva, T.F.S.; da Silva, J.J.R.F.; Pombeiro, A.J.L. Trends in properties of para-substituted 3-(phenylhydrazo)pentane-2,4-diones. *J. Phys. Org. Chem.* **2011**, *24*, 764–773. [CrossRef]

24.   Ribeiro, A.P.C.; Martins, L.M.D.R.S.; Alegria, E.C.B.A.; Matias, I.A.S.; Duarte, T.A.G.; Pombeiro, A.J.L. Catalytic performance of Fe(II)-scorpionate complexes towards cyclohexane oxidation in organic, ionic liquid and/or supercritical CO_2 media: A comparative study. *Catalysts* **2017**, *7*, 230. [CrossRef]

25.   Martins, L.M.D.R.S.; Ribeiro, A.P.C.; Pombeiro, A.J.L. Highly selective cyclohexane oxidation catalyzed by ferrocene in ionic liquid medium. *Lett. Org. Chem.* **2017**, *14*, 571–574. [CrossRef]

26.   Ribeiro, A.P.C.; Martins, L.M.D.R.S.; Hazra, S.; Pombeiro, A.J.L. Catalytic oxidation of cyclohexane with hydrogen peroxide and a tetracopper(II) complex in an ionic liquid. *C. R. Chim.* **2015**, *18*, 758–765. [CrossRef]

27.   Kefini, K.K.; Msagati, T.A.M.; Mamba, B.B. Ferrite nanoparticles: Synthesis, characterization and applications in electronic devices. *Mater. Sci. Eng. B* **2017**, *215*, 37–55. [CrossRef]

28. Alegria, E.C.B.A.; Fontolan, E.; Ribeiro, A.P.C.; Kopylovich, M.N.; Domingos, C.; Ferraria, A.M.; Bertani, R.; Botelho do Rego, A.M.; Pombeiro, A.J.L. Simple solvent-free preparation of dispersed composites and their application as catalysts in oxidation and hydrocarboxylation of cyclohexane. *Mater. Today Chem.* **2017**, *5*, 52–62. [CrossRef]

29. Shul'pin, G.B.; Kozlov, Y.N.; Nizova, G.V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V.S. Oxidations by the reagent "O_2–H_2O_2–vanadium derivative–pyrazine-2-carboxylic acid". Part 12.1 Main features, kinetics and mechanism of alkane hydroperoxidation. *J. Chem. Soc. Perkin Trans.* **2001**, *2*, 1351–1371. [CrossRef]