



Cite this: DOI: 10.1039/c6dt00514d

Received 4th February 2016,
Accepted 16th March 2016

DOI: 10.1039/c6dt00514d

www.rsc.org/dalton

Highly efficient and reusable CNT supported iron(II) catalyst for microwave assisted alcohol oxidation†

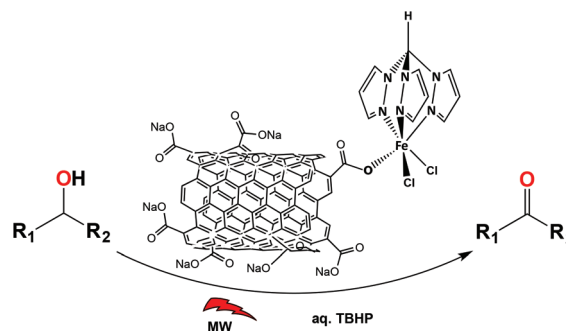
L. M. D. R. S. Martins,^aA. P. C. Ribeiro,^aS. A. C. Carabineiro,^cJ. L. Figueiredo^c and
A. J. L. Pombeiro^a

The highly efficient eco-friendly synthesis of ketones (yields over 99%) from secondary alcohols is achieved by combination of $[\text{FeCl}_2\{\eta^3\text{-HC}(\text{pz})_3\}]$ (pz = pyrazol-1-yl) supported on functionalized multi-walled carbon nanotubes and microwave irradiation, in a solvent-free medium. The carbon homoscorpionate iron(II) complex is the first one of this class to be used as catalyst for the oxidation of alcohols.

Selective alcohol oxidation reactions remain a serious challenge.¹ Despite recent advances,² only a few of the known methods are capable of offering an economic and practical oxidation path towards a particular industrially important transformation. Thus, the development of sustainable catalytic systems, that can mimic Nature's green procedures, is a task of high significance.³

Excellent examples of environmentally friendly and energy-efficient methods concern the naturally occurring iron containing enzymes such as cytochrome P-450 that catalyses *e.g.*, aliphatic and aromatic hydroxylations, and alcohol oxidations.⁴

In this work, we aim to mimic such enzymes for the oxidation of secondary alcohols (using cyclohexanol and 1-phenylethanol as models), employing the bio-inspired tris(pyrazol-1-yl)methane Fe(II) complex $[\text{FeCl}_2\{\eta^3\text{-HC}(\text{pz})_3\}]$ (**1**) supported on functionalized multi-walled carbon nanotubes (**1@MWCNT**) as catalyst in a single-pot, solvent-free protocol. Moreover, environmentally acceptable oxidant (aq. *tert*-butyl hydroperoxide, TBHP) and energy source (microwave irradiation, MW) are used (Scheme 1). The iron compound previously



Scheme 1 Oxidation of secondary alcohols to the corresponding ketones catalysed by $[\text{FeCl}_2\{\eta^3\text{-HC}(\text{pz})_3\}]@MWCNT$.

proved its efficiency in the catalytic partial oxidation of an alkane (cyclohexane),^{5,6} but was not applied for other substrates.

$[\text{FeCl}_2\{\eta^3\text{-HC}(\text{pz})_3\}]$ was prepared and immobilized (2 wt% Fe) on functionalized (oxidised with nitric acid followed by treatment with sodium hydroxide)^{6c,7} MWCNTs.

The immobilization of **1** on the MWCNTs is believed to occur by interaction of the iron(II) centre with the oxygenated functional groups of the MWCNTs surface, with formation of a covalent Fe–O bond,^{6c} providing additional stability of the material in the reaction medium. Far infrared spectrum of **1@MWCNT** (Fig. S1, ESI†) shows that the original $\nu(\text{Fe}-\text{Cl})$ bands⁵ are kept after the anchorage procedure. The morphology of **1@MWCNT** was examined by TEM and SEM (Fig. 1). The presence of black spots at MWCNTs (TEM image, Fig. 1a) can be observed. The EDS (Fig. S2a, ESI†) confirmed the presence of iron. Fig. 1b shows a SEM image of the iron complex supported on MWCNTs. The EDS results, from the same run, also confirmed the presence of iron, proving that the metal is present (see Fig. S2b in ESI†).

The hybrid material **1@MWCNT** was tested as catalyst for the peroxidative oxidation of cyclohexanol and 1-phenylethanol. TBHP (aq., 70% sol.) was used as the typical oxidant under solvent free conditions, although hydrogen peroxide (aq., 30% sol.) was also tested (see Fig. S3, ESI†).

^aCentro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

^bChemical Engineering Department, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Rua Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal. E-mail: lmartins@deq.isel.ipl.pt

^cLCM – Laboratory of Catalysis and Materials, Associate Laboratory LSRE-LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

† Electronic supplementary information (ESI) available: Detailed experimental procedures, analytical and catalytic data. See DOI: 10.1039/c6dt00514d

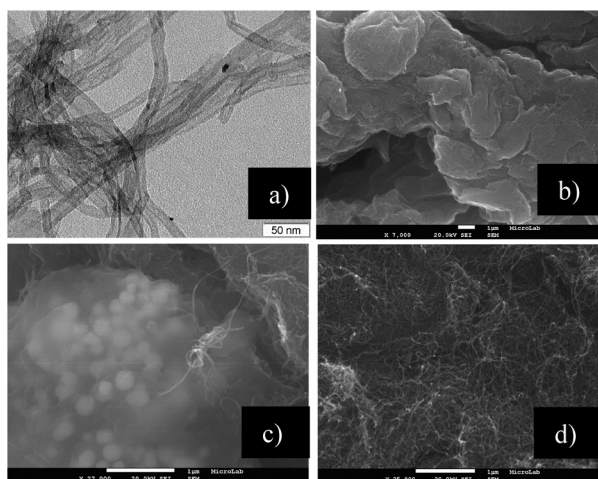


Fig. 1 TEM (a) and SEM (b–d) micrographs of 1@MWCNT. (c) Was obtained after the 5th run and (d) after the 19th run.

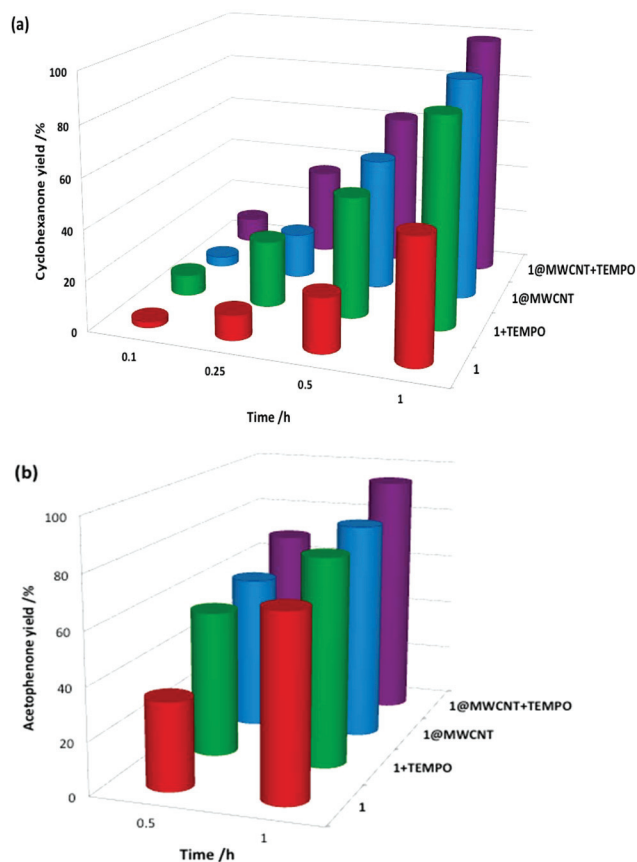


Fig. 2 MW-assisted oxidation of (a) cyclohexanol and (b) 1-phenylethanol with TBHP, at 80 °C, in the presence of 1 or 1@MWCNT (0.1 mol% vs. alcohol).

Quantitative yields of both cyclohexanone and acetophenone (Fig. 2) were achieved after 1 h of MW-assisted oxidation of the corresponding alcohols with TBHP, in the presence of the 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical, by

optimizing reaction conditions (see Fig. 2 for reaction time and TEMPO additive, Fig. S4, ESI[†] for different additives, and Tables S1 and S2, ESI[†]). Control experiments in the absence of 1 (leading to up to 3% or 5% alcohol conversion, for cyclohexanol or 1-phenylethanol respectively, Tables S1, S2 and S4, ESI[†]) confirmed the crucial role of the iron(II) complex to efficiently catalyse the alcohol oxidation.

Moreover, 1@MWCNT maintained its catalytic efficiency to produce cyclohexanone (with a yield over 98%) during five consecutive cycles (Fig. 3; Table S3, ESI[†]) and still retained 80% of its initial activity and concomitant selectivity at the 12th cycle (see also Table S3 and Fig. S5, ESI[†]).

Fig. 1c shows the hybrid material after the 5th recycling run, the iron complex being still attached to the MWCNTs surface. The corresponding EDS results (Fig. S2c, ESI[†]) confirm the presence of iron. Fe 2p XPS (Fig. 4a) spectrum performed on 1@MWCNT after the 5th recycling run shows a mixture of both Fe³⁺ and Fe²⁺ oxidation states, with a predominance of Fe³⁺.

Further measurements were performed for Fe 3p (Fig. 4b), a less intense line. The characteristic peak for Fe³⁺ ions appears at 56 eV.^{8a,c} A lower binding energy peak in Fe 3p spectra at ca. 53 eV (ref. 8c) can be attributed to Fe²⁺ ions while the higher energy (at ca. 60 eV) peak corresponds to Fe³⁺.^{8a} The detected +3 oxidation state of iron at the hybrid material appears to be a consequence of the catalytic process (see below).

The amount of Fe determined by ICP on the carbon catalyst (separated by filtration) sample after the 5th run was 1.9% wt. (*i.e.*, 95% of the initial loading). Thus, 1@MWCNT behaves as a very robust catalyst for MW-assisted alcohols oxidation.

In addition, an efficient ketone synthetic method, leading to higher yields in much shorter times than those achieved by conventional heating, was provided by application of low power MW irradiation that provides rapid initial heating and enhanced reaction rates.⁹ In fact, only 22% of acetophenone was produced after 24 h of reaction under the same reaction conditions (temperature, oxidant:substrate and catalyst:substrate ratios), but with an oil-bath heating. The low yield of ketone obtained was due to the lowering of substrate consumption rate, while the selectivity was maintained.

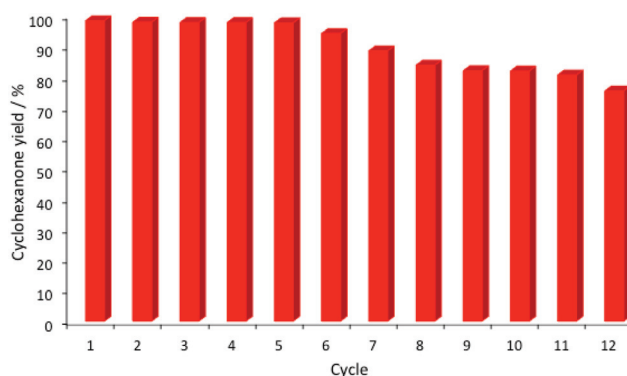


Fig. 3 Effect of the catalyst recycling on the yield of cyclohexanone for the MW-assisted cyclohexanol oxidation (1 h) with TBHP, at 80 °C, catalysed by 1@MWCNT.

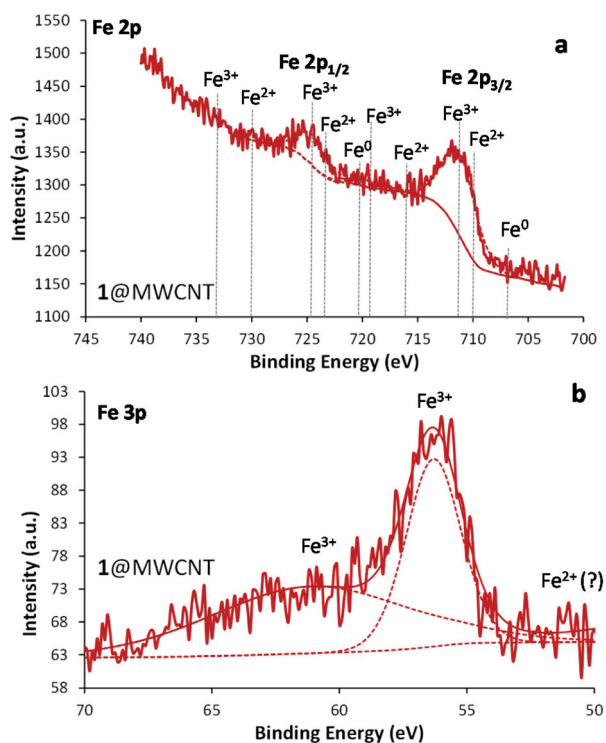


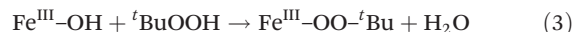
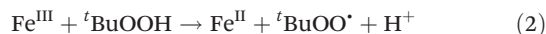
Fig. 4 Fe 2p (a) and Fe 3p (b) XPS spectra of 1@MWCNT. Identification of oxidation states of Fe based on.^{8a,b}

After 19 recycling cycles, extensive iron leaching was detected by EDS (Fig. S2d, ESI†) and ICP (only 0.3 wt% Fe remaining after the 19th run). Also, the increase in the entanglement of the MWCNTs in the SEM image of the material after the 19th run (Fig. 1d) indicates that the surface of the support has been altered.

The immobilization of **1** at functionalized MWCNTs not only provided a more stable, easy to separate and reusable catalyst, but also remarkably improved the catalytic performance of **1** in the homogeneous oxidation of secondary alcohols (only 49% or 70% yields of cyclohexanone or acetophenone from cyclohexanol or 1-phenylethanol, respectively, were achieved after 1 h of MW irradiation in the homogeneous system – Fig. 2; Tables S4 and S2, ESI†).

Although the detailed mechanistic pathway is still to be established, the peroxidative oxidation of the tested secondary alcohols is believed to proceed mainly *via* a radical mechanism involving both carbon- and oxygen-centred radicals, in view of the strong inhibition effect observed when the reaction was carried out in the presence of either the oxygen-radical trap Ph₂NH or the carbon-radical trap CBrCl₃ (entries 17 and 18, respectively of Tables S1 and S4, and entries 11 and 12 of Table S2, ESI†). Moreover, both acid and basic additives showed an inhibitory effect (Fig. S4, ESI†). As previously found by us and others,^{2,10} the mechanism of alcohol oxidation (see below) does not seem to require the presence of protons.

The proposed mechanism may involve ^tBuO[•] and ^tBuOO[•] radicals produced in the Fe promoted decomposition of TBHP,¹¹ according to eqn (1)–(6):



It may also proceed *via* the coordination of the alcohol substrate to an active site of the iron catalyst, and its deprotonation to form the alkoxide ligand, followed by a Fe-centred (and TEMPO assisted) dehydrogenation.¹² The presence of ^tBuOH on the final reaction mixture was detected by GC-MS.

For the iron-assisted steps, a unit change of the metal oxidation state (+2/+3) occurs and the iron centre of **1** appears to be particularly favourable. The stable nitroxyl radical TEMPO alone is not able to directly catalyze the oxidation of alcohols (in particular secondary alcohols) with peroxide,² so its role is to assist the iron catalyst to activate the oxidation agent,¹³ apart from conceivably acting also as a hydrogen-atom abstractor from the alcohol-derived alkoxide ligand.¹²

The catalytic applicability of 1@MWCNT was extended. Other secondary alcohols, either aromatic (*p*-cresol or *o*-cresol) or linear (2- or 3-hexanol), and the primary benzyl alcohol were selectively converted in the corresponding diols (for *p*-cresol and *o*-cresol), ketones (for 2- and 3-hexanol) or aldehydes (for benzyl alcohol) although in considerably lower yields (up to 14%, see Table S5, ESI†). Further optimization of the reaction conditions for these substrates will be attempted in view of the interesting preliminary results achieved.

The immobilization of [FeCl₂{η³-HC(pz)₃}] on functionalized MWCNTs provides an effective route to selectively and quantitatively oxidise secondary alcohols to their corresponding ketones. To our knowledge, this is the first time a C-scorpionate complex is used as a catalyst for alcohol oxidation, either in homogenous or heterogeneous conditions, and constitutes an extension of the catalytic application of biologically inspired metal complexes aiming to reach Nature's sustainability.

Funding from FCT (Fundação para a Ciência e a Tecnologia, Portugal) (UID/QUI/00100/2013, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014 projects) and FEDER (ERDF – European Regional Development Fund) in the framework of Program PT2020 (Project UID/EQU/50020/2013 2013-POCI-01-0145-FEDER-006984) for LSRE-LCM are acknowledged. SACC acknowledges FCT for Investigator 2013 Program (IF/01381/2013/CP1160/CT0007), with financing from the European Social Fund and the Human Potential Operational Program. APCR also acknowledges FCT for the SFRH/BPD/90883/

2012 grant. Dr Carlos Sá (CEMUP) is acknowledged for the assistance with the XPS measurements.

Notes and references

- Q. Cao, L. M. Dornan, L. Rogan, N. L. Hughes and M. J. Muldoon, *Chem. Commun.*, 2014, **50**, 4524.
- M. N. Kopylovich, A. P. C. Ribeiro, E. C. B. A. Alegria, N. M. R. Martins, L. M. D. R. S. Martins and A. J. L. Pombeiro, *Adv. Organomet. Chem.*, 2015, vol. 63, ch. 3, p. 91.
- L. Que, Jr. and W. B. Tolman, *Nature*, 2008, **455**, 333.
- (a) H. Sigel, A. Sigel and R. K. O. Sigel, *The Ubiquitous Roles of Cytochrome P450 Proteins: Metal Ions in Life Sciences*, Wiley, New York, 2007; (b) B. Meunier, S. P. de Visse and S. Shaik, *Chem. Rev.*, 2004, **104**, 3947.
- T. F. S. Silva, E. C. B. A. Alegria, L. M. D. R. S. Martins and A. J. L. Pombeiro, *Adv. Synth. Catal.*, 2008, **350**, 706.
- (a) L. M. D. R. S. Martins and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2014, **265**, 74; (b) L. M. D. R. S. Martins, A. Martins, E. C. B. A. Alegria, A. P. Carvalho and A. J. L. Pombeiro, *Appl. Catal., A*, 2013, **464–465**, 43; (c) L. M. D. R. S. Martins, M. P. Almeida, S. A. C. Carabineiro, J. L. Figueiredo and A. J. L. Pombeiro, *ChemCatChem*, 2013, **5**, 3847.
- M. Peixoto de Almeida, L. M. D. R. S. Martins, S. A. C. Carabineiro, T. Lauterbach, F. Rominger, A. S. K. Hashmi, A. J. L. Pombeiro and J. L. Figueiredo, *Catal. Sci. Technol.*, 2013, **3**, 3056.
- (a) T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, **254**, 2441; (b) M. Descostes, F. Mercier, N. Thromat, C. Beaucaire and M. Gautier-Soyer, *Appl. Surf. Sci.*, 2000, **165**, 288; (c) A. Mekki, D. Holland, C. F. McConville and M. Salim, *J. Non-Cryst. Solids*, 1996, **208**, 267.
- (a) B. Desai and C. O. Kappe, *Immobilized Catalysts*, Springer-Verlag, Berlin, 2004, p. 177; (b) F. Chemat, D. C. Esveld, M. Poux and J. L. Di-Martino, *J. Microwave PowerElectromagn. Energy*, 1998, **33**, 88; (c) D. Bogdal, M. Lukasiewicz, J. Pielichowski, A. Miciak and S. Bednarz, *Tetrahedron*, 2003, **59**, 649.
- (a) M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2015, **301–302**, 200; (b) M. S. Dronova, A. N. Bilyachenko, A. I. Yalymov, Y. N. Kozlov, L. S. Shul'pina, A. A. Korlyukov, D. E. Arkhipov, M. M. Levitsky, E. S. Shubina and G. B. Shul'pin, *Dalton Trans.*, 2014, **43**, 872; (c) M. Sutradhar, L. M. D. R. S. Martins, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Appl. Catal., A*, 2015, **493**, 50.
- (a) L. Feldberg and Y. Sasson, *Tetrahedron Lett.*, 1996, **37**, 2063; (b) V. Mahdavi and M. Mardani, *J. Chem. Sci.*, 2012, **124**, 1107.
- (a) M. V. N. de Souza, *Mini-Rev. Org. Chem.*, 2006, **3**, 155; (b) R. A. Sheldon and I. W. C. E. Arends, *Adv. Synth. Catal.*, 2004, **346**, 1051; (c) P. J. Figiel, A. Sibaouih, J. U. Ahmad, M. Nieger, M. T. Räisänen, M. Leskelä and T. Repo, *Adv. Synth. Catal.*, 2009, **351**, 2625.
- J. M. Hoover, B. L. Ryland and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 2357.