# PhD Open Days

# Mild oxidation of cyclohexane catalyzed by Mn(II)-EDTA functionalized magnetic nanocatalysts

CATALYSIS AND SUSTAINABILITY (CATSUS) FCT-PhD PROGRAM

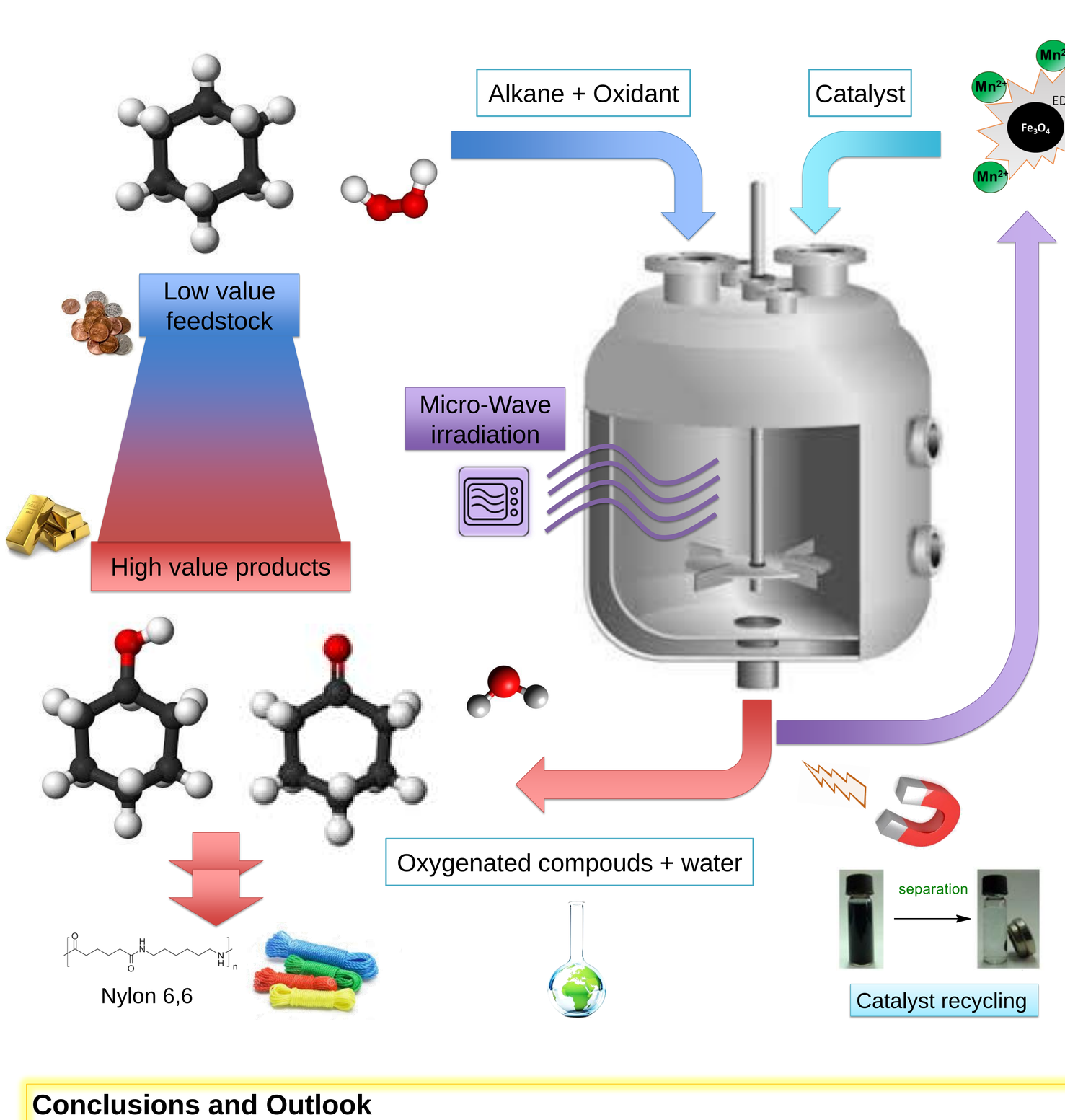
NUNO M. R. MARTINS (nunommartins@tecnico.ulisboa.pt)

http://catsus.tecnico.ulisboa.pt/

http://groups.ist.utl.pt/~cqe.daemon/

## Abstract

Manganese(II) ions combined with ethylenediamine tetraacetic acid (EDTA), as metal-based N,O-chelating ligands, at the surface of ferrite magnetic nanoparticles (MNPs), $Fe_3O_4$@EDTA-$Mn^{2+}$, were prepared by a co-precipitation method and fully characterized by FTIR spectroscopy, powder XRD, SEM, EDS, VSM and TGA.
Those MNPs were applied as alternative selective homogeneous catalysts for the industrially significant oxidation of cyclohexane to cyclohexanol and cyclohexanone. The peroxidative (with tert-butyl hydroperoxide) oxidation of cyclohexane was performed under solvent-free and additive-free conditions and under low-power microwave (MW) irradiation. Cyclohexanol and cyclohexanone were the only products obtained (high selectivity), after 2 h of MW irradiation at 60 ˚C.
Moreover, they have the advantage of being magnetically recoverable catalysts that can be reused in following consecutive runs (up to 5 times).



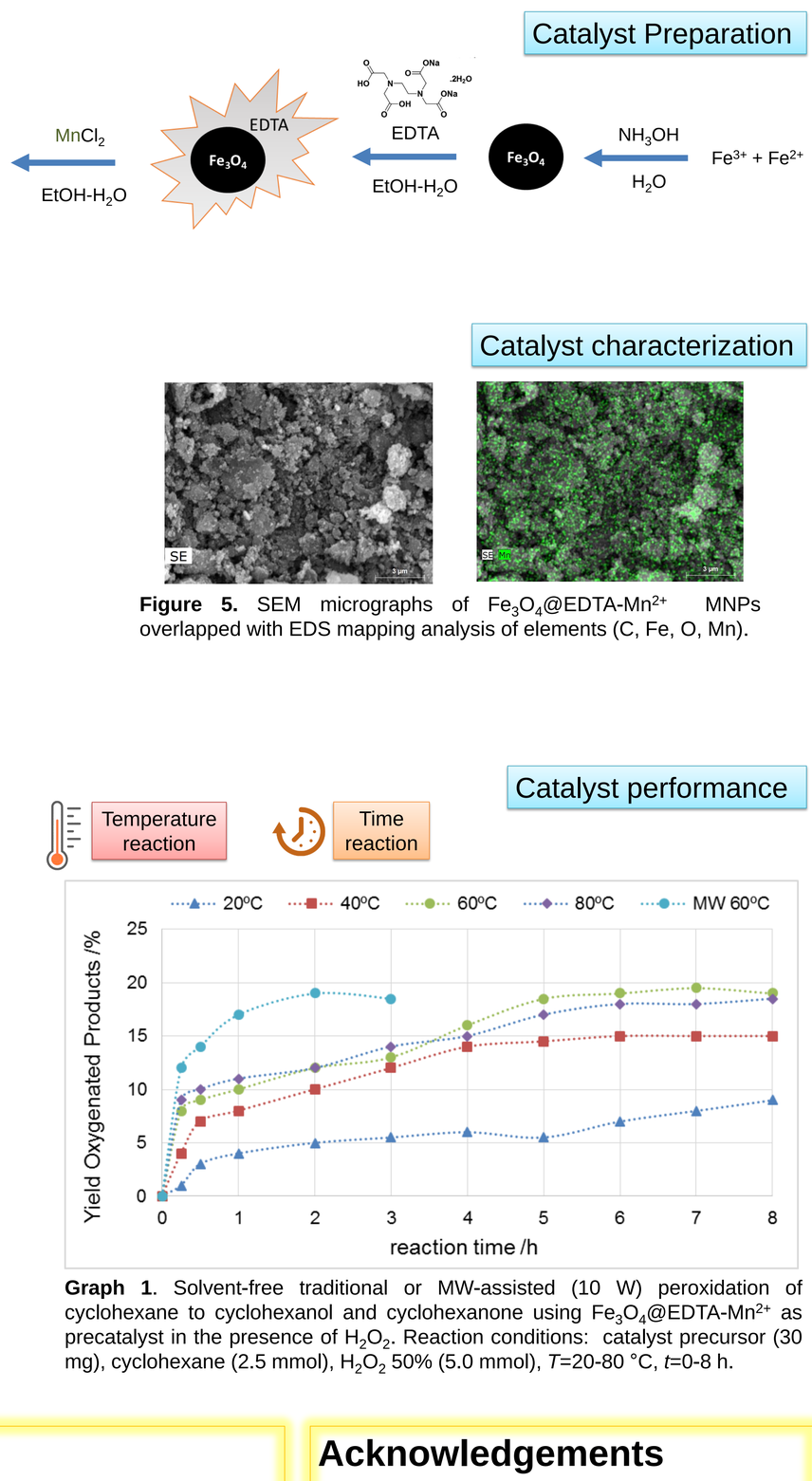




**Figure 5.** SEM micrographs of $Fe_3O_4$@EDTA-$Mn^{2+}$ MNPs overlapped with EDS mapping analysis of elements (C, Fe, O, Mn).

**Graph 1**. Solvent-free traditional or MW-assisted (10 W) peroxidation of cyclohexane to cyclohexanol and cyclohexanone using $Fe_3O_4$@EDTA-$Mn^{2+}$ as precatalyst in the presence of $H_2O_2$. Reaction conditions: catalyst precursor (30 mg), cyclohexane (2.5 mmol), $H_2O_2$ 50% (5.0 mmol), *T*=20-80 °C, *t*=0-8 h.

## Conclusions and Outlook

An efficient solvent-free, mild catalytic, low power microwave-induced oxidation of cyclohexane was achieved, reaching a yield of oxygenated products of 19.4% after 2 h in comparison to 6 h in conventional heating mode. Moreover, corresponding ketones and alcohols were obtained in the presence of a non-hazardous oxidant agent, hydrogen peroxide, in which it is formed water as by-product. Simple preparation of cheap and stable transition metal-based ferrites, use of nontoxic and inexpensive materials, absence of organic solvents, low power (10 W) irradiation for heating, facile separation and recovery of the catalysts from the reaction medium and convenient magnetic recyclability of the catalyst constitutes real advantages of this catalytic system.

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Supervisors: Armando J.L. Pombeiro, Luísa M.D.R.S. Martins, Kamran T. Mahmudov

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