Catalyst for Ketones (KET-CAT) – versatile and sustainable enzyme-inspired C-scorpionate catalysis

A new combination of a Fe (II) complex supported on multi walled carbon nanotubes with microwave radiation in a solvent-free medium resulted in an eco-friendly procedure with ketone yields over 98% (up to 6 consecutive cycles) and TONs up to 1.8 x 10^3.

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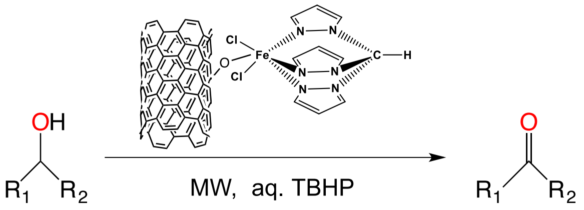
Background:
Selective alcohol oxidation reactions are some of the cornerstones of Chemistry and remain an important challenge. Despite recent advances, only a few of the known methods are capable of offering an economic and practical oxidation towards a particular industrially important transformation. Thus, the development of practical and sustainable catalytic methods, that can mimic Nature's green procedures, is a task of extreme significance nowadays.

The technology:
We aim to replicate naturally occurring iron containing enzymes for the oxidation of secondary alcohols, employing the bio-inspired hydro-soluble C-scorpionate tris(pyrazol-1-yl)methane Fe(II) complex $[FeCl_2\{\eta^3\text{-}HC(pyrazol\text{-}1\text{-}yl)_3\}]$ as catalyst.
By taking advantage of the application of low power microwave (MW) irradiation, an efficient ketone synthetic method was obtained, leading to higher yields in much shorter times than those achieved by conventional heating.



Scheme 1- Oxidation of secondary alcohols to the corresponding ketones in the presence of the C-scorpionate complex $[FeCl_2\{\eta^3\text{-}HC(pyrazol\text{-}1\text{-}yl)_3\}]$ anchored on functionalized multi-walled carbon nanotubes.

In order to combine the catalytic properties of $[FeCl_2\{\eta^3\text{-}HC(pyrazol\text{-}1\text{-}yl)_3\}]$ with the advantages of heterogeneous systems, it was decided to support the complex on functionalized (oxidised with nitric acid followed by a treatment with sodium hydroxide) multi-walled carbon nanotubes. This material outstandingly originated 34% and 70% yields of cyclohexanone and acetophenone, respectively, after 1h of MW-assisted oxidation of the corresponding alcohols (cyclohexanol and 1-phenylethanol), with *t*-butyl hydroperoxide (TBHP). The addition of the 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) radical led to a significant increase of the cyclohexanone yield to 98.3%, while maintaining the selectivity.

Benefits:
This catalysis process produces the same results as other more "aggressive" methods, but with fewer catalyst quantities, less additives, less oxidants and no solvents at all. It also requires less reaction time (just 1 hour) and is easier to prepare.
The catalyst is reusable for several cycles, easy to separate from the reagents and produces fewer by-products. It is more active in the oxidation of aliphatic alcohols, and, while being a heterogeneous catalyst, as selective and active as the homogeneous ones.
Overall, this new method is less expensive, more productive and environmentally greener than conventional ones.

Potential Commercial Use / Applications:
Ketones have practical applications such as industrial solvents, as diluents in lacquers, paints and plastics, in the textile industry, in wool and for cleaning. Other uses of ketones are in synthetic fibers, car interiors, additives for plastics, fragrances and cosmetics, pharmaceuticals and synthetic supplements such as vitamins, etc.
This technology is useful for chemical companies, namely ketones producers, and fine chemistry companies, that normally do not use many catalysts. Their activity results, therefore, in many by-products (up to 100Kg per 1Kg of final product) and a large ecological footprint.
KET-CAT adds a cost saving, green chemistry perspective to this sector. Its TRL - technology readiness level is 4.

Cooperation Options:
Licensing agreement.
Research Partnership.

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