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Iron Triflate Salts as Precursors of Highly Active and Selective Catalyst for the Solvent-Free Oxidation of Cyclohexane

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PURPOSE OF THE ABSTRACT

The oxidation of cyclohexane (CyH) to cyclohexanol (CyOH) and cyclohexanone (CyONE), also termed as KA oil, is a well-known industrial process for the production of adipic acid.[1] This process comprises two consecutive oxidation steps: (i) non-catalytic autooxidation of CyH by O₂ yielding cyclohexyl hydroperoxide (CyHP), and (ii) deperoxidation of CyHP to KA oil catalyzed by a transition metal, typically a homogeneous cobalt catalyst, under a radical chain mechanism. The process is conducted at very low CyH conversion (~5%) with a CyHP selectivity of 60-70% in the first step. The industrial challenge is to increase the conversion and KA selectivity while keeping the CyHP concentration as low as possible using a clean and safe route. In this view, a fast and selective catalytic pathway using a non-toxic metal would be desirable.

High-valent iron-oxo complexes can efficiently catalyze oxidation reactions in living systems. Iron-oxo systems have been extended to non-heme bio-inspired catalysts based on Fe centers, and to mononuclear iron complexes.[2] Herein we report an unprecedented high catalytic activity of Fe II (OTf)₂ and Fe III (OTf)₃ (TOF > 10,000 h⁻¹) for CyH oxidation towards KA oil using TBHP as oxidant in the absence of ligand. Both salts behaved as precursors of active iron species for CyH oxidation during the reaction. We provide detailed insight into the structure of the catalyst under the reaction conditions by combining electron paramagnetic resonance (EPR) and DFT calculations.

FIGURES

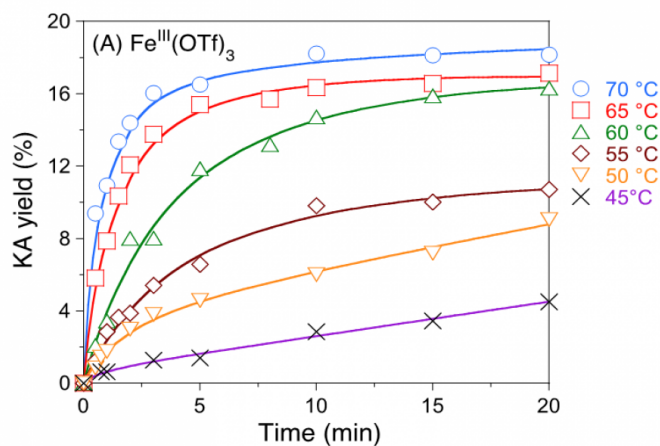


FIGURE 1

Kinetics of KA oil production in CyH oxidation catalyzed by Fe III (OTf) 3 with TBHP as oxidant. Reaction conditions: 45-70 C, 0.14 mM catalyst (10 ppm Fe), 4 g of CyH containing 7.5 wt.% TBHP, 0-20 min.

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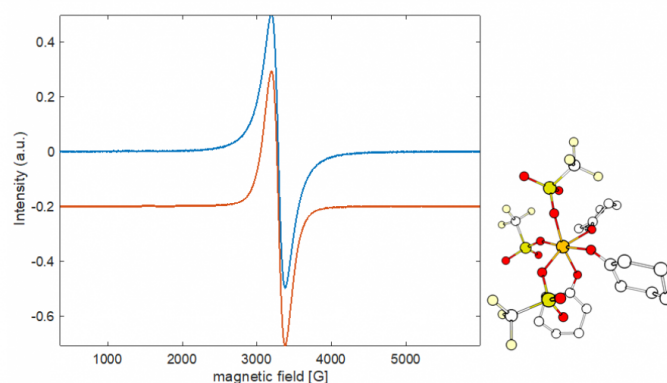


FIGURE 2

Experimental (blue) and simulated (red) EPR spectra of $\text{Fe}^{\text{III}}(\text{OTf})_3$ (10 mM) in CyH in the presence of CyONE (10 equiv).

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KEYWORDS

EPR | oxidation | iron | triflate

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