

Title: Pyrazole or tris(pyrazolyl)ethanol oxo-vanadium(IV) complexes as homogeneous or supported catalysts for oxidation of cyclohexane under mild conditions

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Abstract: The oxovanadium(IV) complexes [VO(acac)(2)(Hpz)].HC(pz)(3) 1.HC(pz)(3) (acac= acetylacetonate, Hpz = pyrazole, pz = pyrazolyl) and [VOCl2{HOCH2C(pz)(3)}] 2 were obtained from reaction of [VO(acac)(2)] with hydrotris(1-pyrazolyl)methane or of VCl(3)with 2,2,2-tris(1-pyrazolyl)ethanol. The compounds were characterized by elemental analysis, IR, Far-IR and EPR spectroscopies, FAB or ESI mass-spectrometry and, for 1, by single crystal X-ray diffraction analysis. 1 and 2 exhibit catalytic activity for the oxidation of cyclohexane to the cyclohexanol and cyclohexanone mixture in homogeneous system (TONS up to 1100) under mild conditions (NCMe, 24h, room temperature) using benzoyl peroxide (BPO), tert-butyl hydroperoxide (TBHP), m-chloroperoxybenzoic acid (mCPBA), hydrogen peroxide or the urea-hydrogen peroxide adduct (UHP) as oxidants. 1 and 2 were also immobilized on a polydimethylsiloxane membrane (1-PDMS or 2-PDMS) and the systems acted as supported catalysts for the cyclohexane oxidation using the above oxidants (TONs up to 620). The best results were obtained with mCPBA or BPO as oxidant. The effects of various parameters, such as the amount of catalyst, nitric acid, reaction time, type of oxidant and oxidant-to-catalyst molar ratio, were investigated, for both homogeneous and supported systems. (C) 2012 Elsevier B.V. All rights reserved.

Author Keywords: Cyclohexane; C-scorpionates; Vanadium; Homogeneous catalysis; Oxidation; Crystal structure; Supported catalysis

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