Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Dysprosium-doped zinc tungstate nanospheres as highly efficient heterogeneous catalysts in green oxidation of terpenic alcohols with hydrogen peroxide

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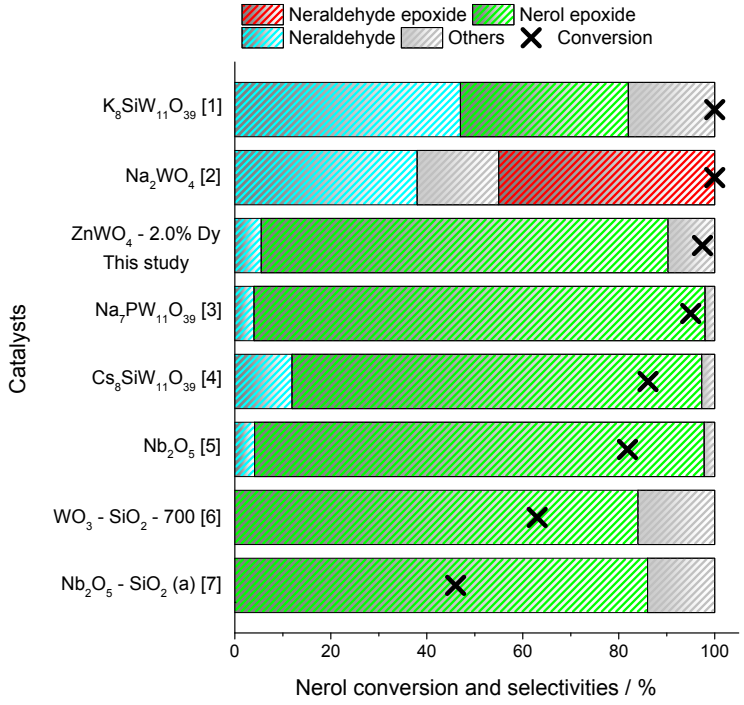
SUPPLEMENTAL MATERIAL



Ref.1 - Nerol:H_2O_2 (1:3); Catalyst (1.3 mol %); solvent DMA; 3 h; 363 K
Ref. 2 - Nerol:H_2O_2 (1:2); Catalyst (1.3 mol %); solvent DMA; 4 h; 363 K
This study - Nerol:H_2O_2 (1:2); Catalyst (3.5 mol %); solvent ACN; 8 h; 333 K
Ref. 3 - Nerol:H_2O_2 (1:1); Catalyst (0.3 mol %); solvent ACN; 4 h; 298 K
Ref. 4 - Nerol:H_2O_2 (1:2); Catalyst (4.0 mol %); solvent ACN; 8 h; 333 K
Ref. 5 - Nerol:H_2O_2 (1:2); Catalyst (4.0 mol %); solvent ACN; 8 h; 333 K
Ref. 6 - Nerol:H_2O_2 (1:1); Catalyst (3.4 mol %); solvent - ACN; 2 h; 343 K
Ref. 7 - Nerol:H_2O_2 (1:2); Catalyst (4.6 mol %); solvent MeOH; 5 h; 343 K

Fig SM1. Comparison of conversion and selectivity of nerol oxidation with hydrogen peroxide over different solid catalysts

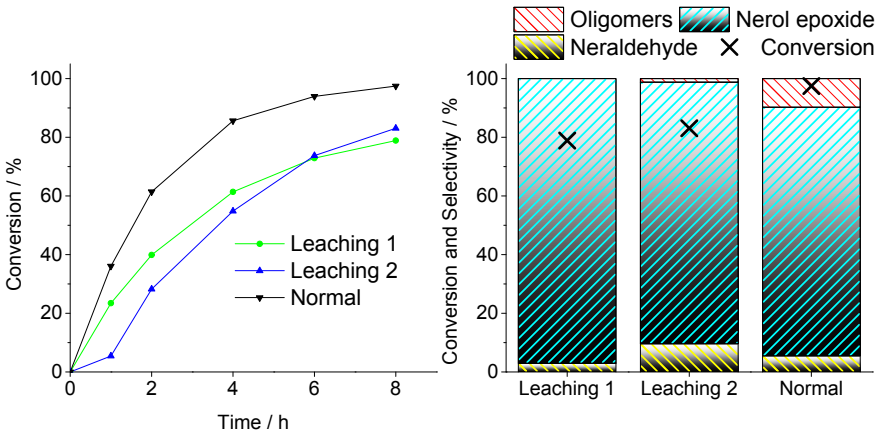


Fig. SM2 Conversion and selectivity of nerol oxidation reactions with H_2O_2 in the presence of $ZnWO_4$ - 2.0% Dy catalyst[a]

[a]*Reaction conditions:* nerol (1.375 mmol), H_2O_2 (2.750 mmol), temperature (333 K), catalyst (15 mg), CH_3CN (10 mL), time (8 h)

Leaching 1: Stirring 30 min (catalyst + solvent); after that, the catalyst was removed by centrifugation and the substrate and hydrogen peroxide were placed in the reaction medium; the reaction was followed for 8 h with aliquots periodically collected.

Leaching 2: all components were placed in the reaction medium for 30 min under stirring; after this time, the catalyst was removed by centrifugation and the reaction proceeded normally until 8 h was completed.

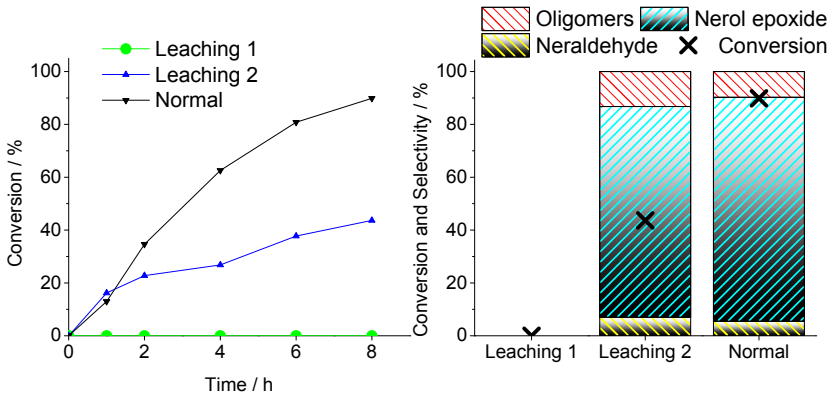


Fig. SM3 Conversion and selectivity of nerol oxidation reactions with H_2O_2 in the presence of $ZnWO_4$ catalyst[a]

[a]*Reaction conditions:* nerol (1.375 mmol), H_2O_2 (2.750 mmol), temperature (333 K), catalyst (15 mg), CH_3CN (10 mL), time (8 h)

Leaching 1: Stirring 30 min (catalyst + solvent); after that, the catalyst was removed by centrifugation and the substrate and hydrogen peroxide were placed in the reaction medium; the reaction was followed for 8 h with aliquots periodically collected.

Leaching 2: all components were placed in the reaction medium for 30 min under stirring; after this time, the catalyst was removed by centrifugation and the reaction proceeded normally until 8 h was completed.

NEROL PRODUCTS

Nerol epoxide

EIMS 70 eV, *m/z* (rel. int. %): 170 $[M]^+$ (1), 152 (1), 137 (1), 109 (67), 95 (27), 82 (40), 69 (65), 67 (68), 55 (35), 43 (89), 41 (100).

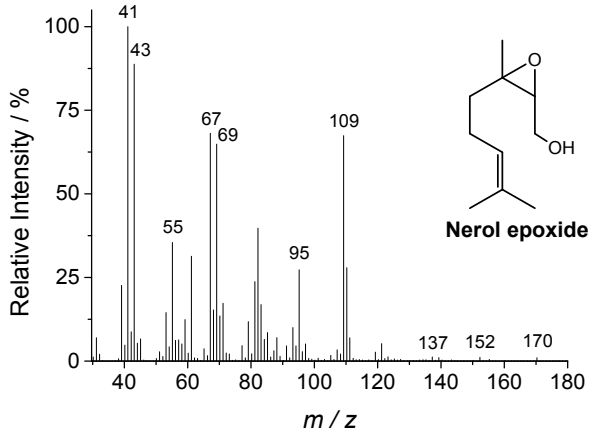


Fig. SM2 Mass spectrum of nerol epoxide[1]

Neraldehyde

EIMS 70 eV, *m/z* (rel. int. %): 152 $[M]^+$ (1), 94 (27), 84 (24), 69 (80), 53 (14), 41 (100), 39 (23).

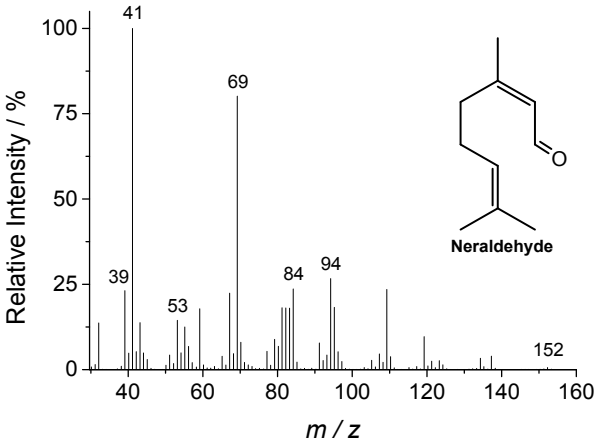


Fig. SM3 Mass spectrum of neraldehyde[2,3]

BORNEOL PRODUCT

Camphor

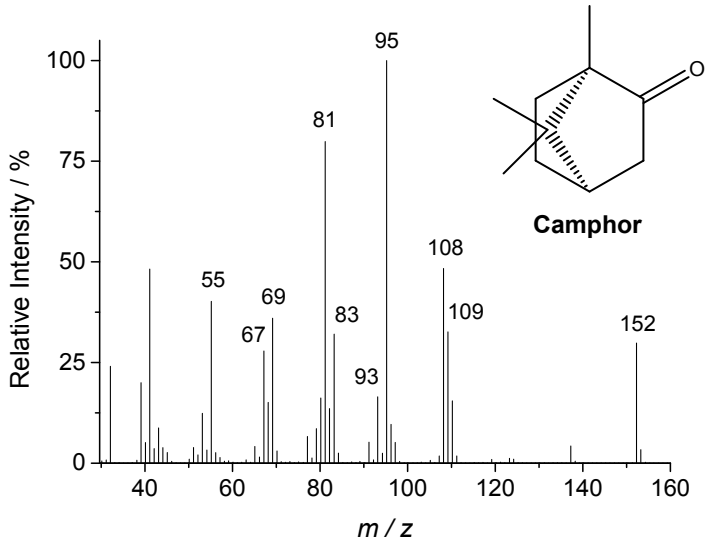


Fig. SM4 Mass spectrum of camphor[4]

GERANIOL PRODUCTS

Geraniol diepoxide

EIMS 70 eV, *m/z* (rel. int. %): 186 $[M]^+$ (1), 155 (1), 125 (9), 111 (10), 93 (7), 84 (29), 71 (30), 59 (22), 43 (100).

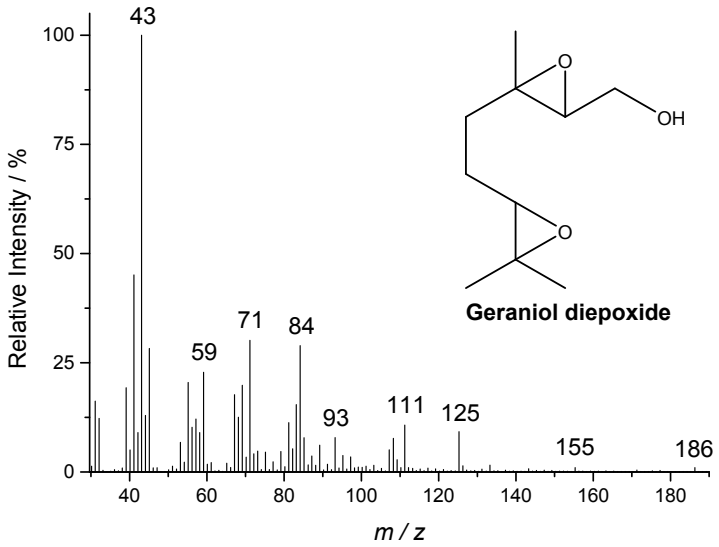


Fig. SM5 Mass spectrum of geraniol diepoxide[1]

Geraniol epoxide

EIMS 70 eV, *m/z* (rel. int. %): 152 $[M-H_2O]^+$ (0.7), 137 (1), 109 (57), 97 (5), 85 (7), 81 (24), 71 (18), 67 (65), 59 (11), 57 (6), 55 (40), 43 (90), 41 (100).

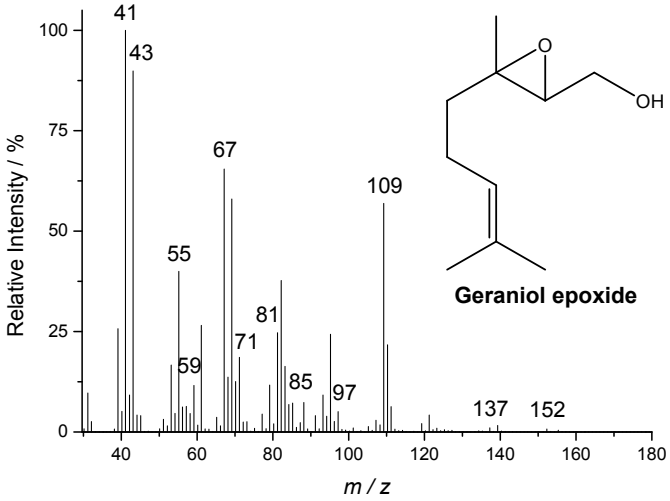


Fig. SM6 Mass spectrum of geraniol epoxide[1]

Geranaldehyde

EIMS 70 eV, *m/z* (rel. int. %): 152 $[M]^+$ (3), 137 (7), 94 (13), 84 (24), 69 (94), 41 (100).

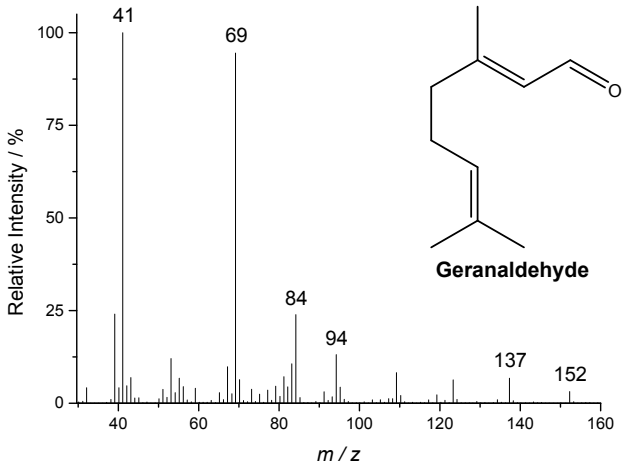


Fig. SM7 Mass spectrum of geranaldehyde[3]

α-TERPINEOL PRODUCTS

p-menthan-2-ol, 1,8-epoxy

EIMS 70 eV, *m/z* (rel. int. %): 170 $[M]^+$ (10), 126 (50), 108 (79), 71 (56), 43 (100), 41 (33).

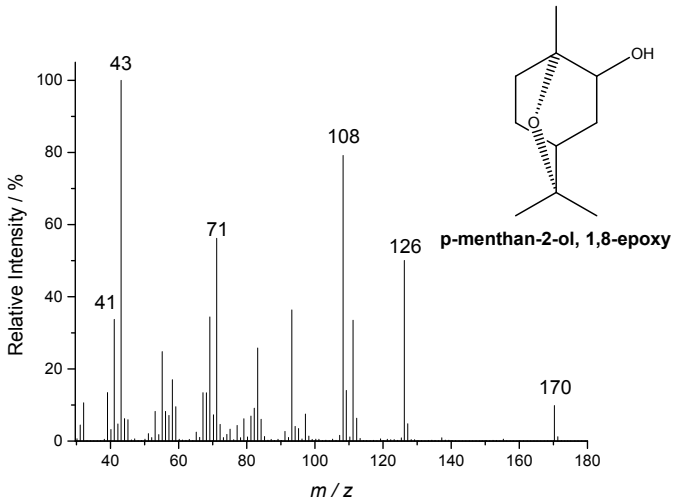


Fig. SM8 Mass spectrum of p-menthan-2-ol, 1,8-epoxy[5]

α-Terpineol epoxide

EIMS 70 eV, *m/z* (rel. int. %): 170 $[M]^+$ (0.1), 71 (69), 59 (60), 43 (100), 41 (26).

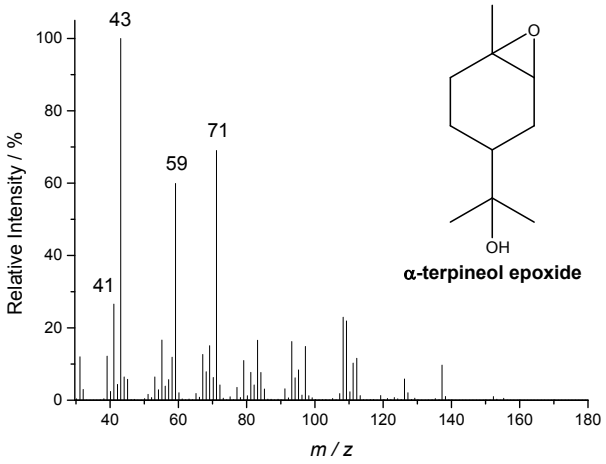


Fig. SM9 Mass spectrum of α-terpineol epoxide[5]

References used in Fig.SM1.

1. Silva M J, Andrade P H S, Ferreira S O, Vilanculo C B, Oliveira C M O (2018) Monolacunary $K_8SiW_{11}O_{39}$-Catalyzed Terpenic Alcohols Oxidation with Hydrogen Peroxide. Catal Lett 148:2516-2434

2. Viana L A S, Silva G R N, Silva M J (2018) A Highly Selective Na_2WO_4-Catalyzed of Terpenic Alcohols by Hydrogen Peroxide. Catal Lett 148:374-386

3. Vilanculo C B, Silva M J (2020) Unraveling the role of the lacunar $Na_7PW_{11}O_{39}$ catalyst in the oxidation of terpene alcohols with hydrogen peroxide at room tempearature. New J Chem 44:2813-2820

4. Batalha D C, Ferreira S O, Silva R C, Silva M J (2020) Cesium-Exchanged Lacunar Keggin Heteropolyacid Salts: Efficient Solid Catalyst for the Green Oxidation of Terpenics Alcohols with Hydrogen Peroxide. ChemSelect 5:1976:1986

5. Batalha D C, Marins N H, Silva R C, Carreño N L V, Farjado H V, Silva M J (2020) Oxidation of terpenic alcohols with hydrogen peroxide promoted by Nb_2O_5 obtained by microwave-assisted hydrothermal method. Mol Catal 489:110941:110952

6. Somma, F., & Strukul, G. (2004). Oxidation of geraniol and other substituted olefins with hydrogen peroxide using mesoporous, sol–gel-made tungsten oxide–silica mixed oxide catalysts. J. Catal., 227(2):344.

7. Somma, F., Canton, P., & Strukul, G. (2005). Effect of the matrix in niobium-based aerogel catalysts for the selective oxidation of olefins with hydrogen peroxide. J. Catal., 229(2): 490.