A Novel and Catalytically Active Boron Peroxotungstate

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Introduction

It is known that the reaction of hydrogen peroxide with certain metals (e.g. Mo^{VI}, W^{VI}, V^{V}) yield peroxocomplexes, which are efficient oxidation catalysts in the presence of H_2O_2 [1,2], namely $\{(XO_4)[W(O)(O_2)_2]_4\}^{3-}$, the so-called Venturello peroxocomplex [3], where X = P or As, and $[M_2O_3(O_2)_4]^{2-}$ [4]. Almost all of them have been studied in the epoxidation of olefins [4-7]. Several groups have used the Venturello peroxocomplex or related systems involving namely $[XW_nO_x]^{m-}$ peroxocomplexes, X = S, As [8]. However, to our knowledge, no one have described any peroxocomplex containing boron.
All the tungsten peroxocomplexes known have been tested in the epoxidation of cyclic and linear alkenes with H_2O_2 in homogeneous conditions. There are some peroxocomplexes, with several transition metals, like V^{V}, capable of oxidizing alkanes [9]. However, there is only one report on the use of tungsten peroxocomplexes in the oxidation of alkanes [10].
We will present the results obtained in the homogeneous and heterogeneous oxidation of *cis*-cyclooctene, several terpenes and cyclooctane with H_2O_2 as oxidant, in acetonitrile, catalysed by the benzyltributylammonium (BTBA) salt of the peroxocomplex $(BTBA)_4H[BW_4O_{24}]$.

Experimental

The peroxocomplex $(BTBA)_4H[BW_4O_{24}]$ was prepared by mixing an aqueous solutions of $Na_2WO_4.2H_2O$ and 30% H_2O_2 with pH adjustment to 2.8 with HCl 6 M, followed by the addition of boric acid and benzyltributylammonium chloride. The prepared peroxocomplex was immobilized using as support a metal-organic framework with large cavities (MOF-BW4). The peroxocomplex was incorporated inside of this mesoporous hybrid material. The peroxocomplex and the material MOF-BW4 were analyzed by infrared, Raman and NMR spectroscopies, powder X-ray diffraction, elemental and thermogravimetric analyses. For analysis of the reaction products, FID gas chromatography and gas chromatography-mass spectrometry (capillary column: DB-5 type, 30 m x 0.25 mm i.d., 0.25 μm film thickness) were used.

Results/Discussion

A new peroxocomplex containing boron was synthesized and incorporated into a metal-organic framework. The oxidation results obtained in homogeneous medium are summarized in table 1 and will be compared with the ones obtained under heterogeneous conditions. The recyclability and the bleaching of the heterogeneous catalyst will be discussed.

Table 1. Oxidation results in the presence of $(BTBA)_4H[BW_4O_{24}]$ with H_2O_2 under homogeneous conditions.

Substrate	Time (h)	Conversion (%)	TON
cis-Cyclooctene	6	76	456
Geraniol	5	86	286
Limonene	24	99	330
Linalool	5	93	310
Cyclooctane	12	100	667

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