



Osmium impregnated on magnetite as a heterogeneous catalyst for the *syn*-dihydroxylation of alkenes

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ABSTRACT

A new catalyst derived from osmium has been prepared, fully characterized and tested in the dihydroxylation of alkenes. The catalyst was prepared by wet impregnation methodology of $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ on a commercial micro-magnetite surface. The catalyst allowed the reaction with one of the lowest osmium loadings for a heterogeneous catalyst and was selective for the monodihydroxylation of 1,5-dienes. Moreover, the catalyst was easily removed from the reaction medium by the simple use of a magnet. The selectivity of catalyst is very high with conversions up to 99%. Preliminary kinetics studies showed a first-order reaction rate with respect to the catalyst.

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1. Introduction

The *syn*-dihydroxylation of alkenes for the preparation of diols [1,2] is one of the most explored reactions in organic chemistry due to the importance of these compounds for the fine chemical industry and their use as intermediates for pharmaceuticals and agrochemicals. The most employed catalyst for this transformation is OsO_4 , with the asymmetric version of this reaction being performed using the appropriated chiral ligands [3–6]. The use of the aforementioned oxide has important drawbacks such as the high cost, its high volatility and its toxicity, which limits or makes very difficult its application in industry, and in the laboratory.

In the last years a great effort has been made to prepare heterogeneous catalysts [7–11] which overcome these problems. Different supports having osmium salts in different loadings (osmium/support ratio), such as polymers (0.25–5 mol%) [12–15], silica (0.25 mol%) [16], cinchona modified silica gel (1 mol%) [17–19], hydrotalcites (8.5 mol%) [20,21], dendrimers (0.25–1 mol%) [22,23], polysiloxane (1 mol%) [24], imigolite (0.25 mol%) [25] fullerenes (3.8 mol%) [26], magnetically recoverable quaternary ammonium salts (2 mol%) [27], or zeolites (0.6 mol%) [28] have been reported for this purpose, as well as other strategies including microencapsulation (5 mol%) [29–31], ion-exchange technique (0.5–2.5 mol%) [32–35], and the use of poly(ethylene glycol) (0.5 mol%) [36] or ionic liquids (0.5–2 mol%)

[37,38]. The majority of these catalyst preparation strategies suffer the need of a large and complicated work in the corresponding catalyst elaboration, so the initial interest has not been transformed into general industrial applications.

We have recently developed a new, simple and robust method to immobilize different metal oxides [39–48] on the surface of the magnetite [49–51]. Here, we show the effective application of this new osmium impregnated on magnetite catalyst in organic synthesis for the *syn*-dihydroxylation of alkenes.

2. Experimental

2.1. General procedure for the preparation of catalyst

To a stirred solution of $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ (349 mg, 1 mmol) in deionized water (120 mL) was added Fe_3O_4 (4 g, 17 mmol, powder <5 μm , BET area: 9.86 m^2/g). After 10 min at room temperature, the mixture was slowly basified with NaOH (1 M) until pH around 13. The mixture was stirred during one day at room temperature. After that, the catalyst was filtered under vacuum and washed several times with deionized water (3×10 mL). The solid was dried at 100 °C during 24 h in a standard glassware oven, obtaining the expected catalyst.

2.2. Characterization of catalyst

XRD patterns were recorded on a Bruker D8 advance diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) at a setting of 40 kV and 40 mA. TEM images were obtained on a JEOL

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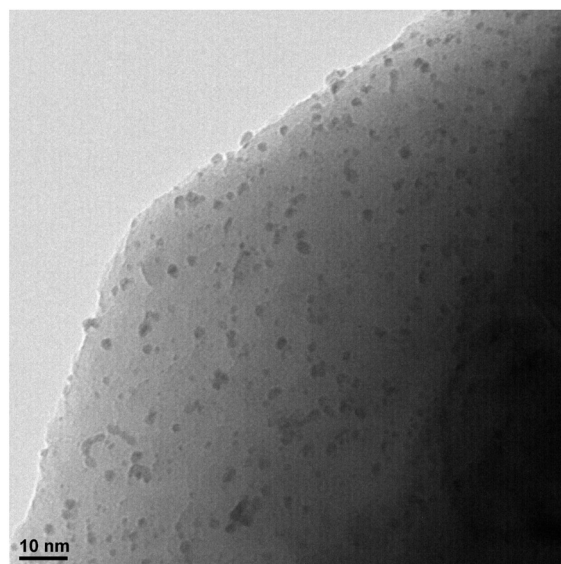
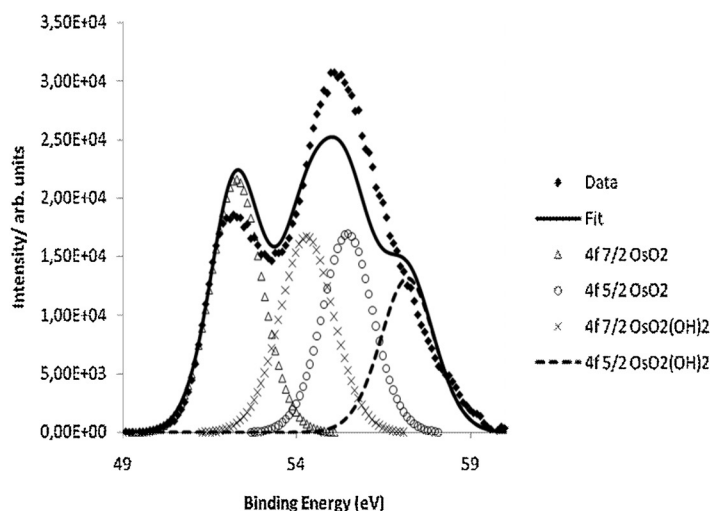


Fig. 1. X-Ray photoelectron spectroscopy and TEM image of the fresh osmium impregnated magnetite catalyst.

JEM-2010 electron microscope equipped with an X-ray detector for microanalysis (EDS). XRF analyses were obtained on a X-ray spectrometer PHILIPS MAGIX PRO equipped with a rhodium X-ray tube and a beryllium window. Surface areas were determined by the application of the BET equation to N_2 adsorption isotherm at 77 K. Adsorption data were obtained from a QUANTACROME AUTOSORB-6 equipment.

2.3. General procedure for the dihydroxylation of alkenes

To a stirred solution of alkene (**1**, 1 mmol) in a mixture of acetone:H₂O 2:1 (3 mL) in a pressure tube, OsO₂–Fe₃O₄ (10 mg, 0.08% of osmium) and NMO (234 mg, 2 mmol) were added. The resulting mixture was stirred at 100 °C during 3 h. The catalyst was removed by a magnet and the resulting solution was extracted with ether. The organic phases were dried over MgSO₄, and the solvents were removed under reduced pressure. The product was usually purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **2** or **4**. Physical and spectroscopic data as well as literature for all compounds are included as [Appendices A and B](#). FT-IR spectra were obtained on a Nicolet impact 400D spectrophotometer. NMR spectra were recorded on a Bruker AC-300 apparatus (300 MHz for ¹H and 75 MHz for ¹³C) using CDCl₃ as a solvent and TMS as internal standard for ¹H and ¹³C; chemical shifts are given in δ (parts per million) and coupling constants (*J*) in Hertz. Mass spectra (EI) were obtained at 70 eV on a spectrometer Agilent GC/MS-5973N, giving fragment ions in *m/z* with relative intensities (%) in parentheses. Thin layer chromatography (TLC) was carried out on DC-Fertigfolien ALUGRAM plates coated with a 0.2 mm layer of silica gel; detection by UV₂₅₄ light, staining with phosphomolybdic acid [25 g phosphomolybdic acid, 10 g Ce(SO₄)₂·4H₂O, 60 mL of concentrated H₂SO₄ and 940 mL H₂O]. Column chromatography was performed using silica gel 60 of 35–70 mesh.

3. Results and discussion

3.1. Synthesis of catalyst

The catalyst was easily prepared by the typical wet impregnation methodology. The addition of commercial micro-particles of magnetite to an aqueous solution of OsCl₃, followed by the

increasing of the pH of the solution up to nearly 13 by addition of 2 M aqueous solution of NaOH, filtering, washing with water and evaporation of water at 100 °C during 24 h rendered the catalyst (non osmium species were detected in the aqueous mixture, coming from the evaporated phase, which was collected in a liquid nitrogen trap). The XRD analysis of freshly prepared catalyst did not provide any concluding information due to the low metal osmium loading and its high dispersion, with exception of the support diffraction peaks (Fe₃O₄, see [Appendices A and B](#)). The total incorporation of osmium was around 1.6%, according to the XRF and the BET area surface was 8.6 m²/g, almost the same as in the starting magnetite (9.8 m²/g). The distribution of osmium particles seems to be homogenous on the surface of magnetite, according to the TEM images ([Fig. 1](#)), and the size distribution was 1.7 ± 0.6 nm. The XPS spectra showed the presence of two osmium species in a nearly 1:1 mixture, and these species seemed to be OsO₂ and OsO₂(OH)₂ according to the binding energies ([Fig. 1](#))[\[52\]](#).

3.2. Dihydroxylation reactions

Once the catalyst was prepared and fully characterized, we faced the problem of their activity in dihydroxylation processes. Initial studies were performed upon the reaction of (*E*)-1-phenylprop-1-ene (**1a**) with 4-methylmorpholine *N*-oxide (NMO), as the oxidant, in a mixture of solvents (acetone/H₂O: 2/1) at 70 °C and the effects of different parameters were evaluated ([Table 1](#)). First, the effect of the temperature of the reaction was studied (entries 1–4). When the temperature was reduced to 50 °C the reaction took place, although it needed a longer reaction time to achieve similar yield. The increase of the temperature to 100 °C allowed to obtain the corresponding diol **2a** in 72% yield in only 3 h (entry 3). However, a further increase on the temperature gave similar results (entry 4). Then, other solvents were tested in the reaction (entries 5–7), but the initial mixture of acetone:H₂O gave the best results. Only in the case of using toluene, it was possible to obtain the diol **2a** in modest yield (entry 7). The reaction failed when other oxidants, such as *t*-BuOOH, H₂O₂, or isoquinoline *N*-oxide, were used. Only using trimethylamine *N*-oxide similar result was obtained (entry 10). The importance of the amount of oxidant was also evaluated (entries 12 and 13). When the amount of the oxidant was increased to 200 mol% the corresponding diol was obtained in 97% yield in only 1 h. However, increasing the amount of the oxidant to 300 mol%

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