

Elsevier Editorial System(tm) for Applied Catalysis A
Manuscript Draft

Manuscript Number: APCATA-D-13-00876R2

Title: Osmium Impregnated on Magnetite as a Heterogeneous Catalyst for the syn-Dihydroxylation of Alkenes

Article Type: Research Paper

Keywords: Heterogeneous catalyst
dihydroxylation process
magnetite
osmium oxide

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Alicante, October 23th, 2013

Dear Prof Lopez Nieto

Please, find attached our manuscript entitled “Osmium Impregnated on Magnetite as a Heterogeneous Catalyst for the *syn*-Dihydroxylation of Alkenes”, which has been changed (highlighted in yellow in the text) according to the reviewers’ comments as follows:

Reviewer 1:

Reviewer 2:

The mistakes “fully” (page 1, line 8), “been” and “into” (page 2, line 21) have been corrected.

Page 5, Line 13: the term “of the initial charged osmium.” has been added

Page 9, Line -2: The word “not” has been added

Editor:

External box in all figures has been removed.

The former Figure 2 has been split into two new Figures 2 and 3.

Finally, we would like to thank the reviewers and you, once again, for their careful work and helpful comments.

Sincerely yours,

Diego J. Ramón

Professor of Organic Chemistry

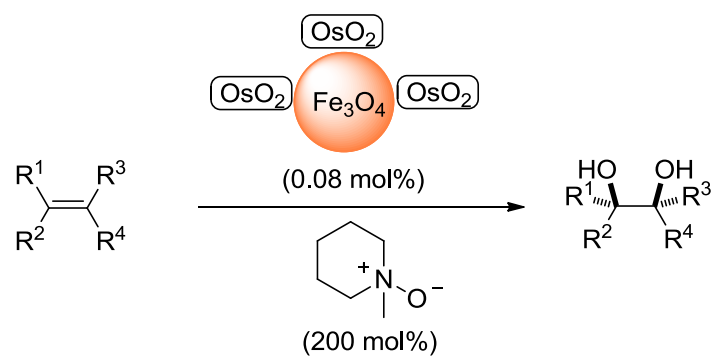
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Graphical abstract



Highlights

Easy preparation of a novel magnetic nanocatalyst.

Simple catalyst removing by an external magnetic field.

The lowest catalyst loading reported for this transformation

The use of complicated and expensive organic ligands, used in related processes, is avoided

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.

Keywords

Heterogeneous catalyst, dihydroxylation process, magnetite, osmium oxide

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 OsO₄, 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[37-46] on the surface of the magnetite[47-49]. 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 OsCl₃•3H₂O (349 mg, 1 mmol) in deionized water (120 mL) was added Fe₃O₄ (4 g, 17 mmol, powder < 5 μm, BET area: 9.86 m²/g). After 10 minutes at room temperature, the mixture was slowly basified with NaOH (1M) 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 x 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 Cu K α radiation ($\lambda = 0.15406$ nm) at a setting of 40 kV and 40 mA. TEM images were obtained on a JEOL 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 N₂ adsorption isotherm at 77K. 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 hours. 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 Supplementary data. 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)₂·4 H₂O, 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 2M 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 (Fe_3O_4 , see supporting data). The total incorporation of osmium was around 1.6%, according to the XRF and the BET area surface was $8.6 \text{ m}^2/\text{g}$, almost the same as in the starting magnetite ($9.8 \text{ m}^2/\text{g}$). The distribution of osmium particles seems to be homogenous on the surface of magnetite, according to the TEM images (Figure 1), and the size distribution was $1.7 \pm 0.6 \text{ nm}$. The XPS spectra showed the presence of two osmium species in a nearly 1:1 mixture, and these species seemed to be OsO_2 and $\text{OsO}_2(\text{OH})_2$ according to the binding energies (Figure 1)[52].

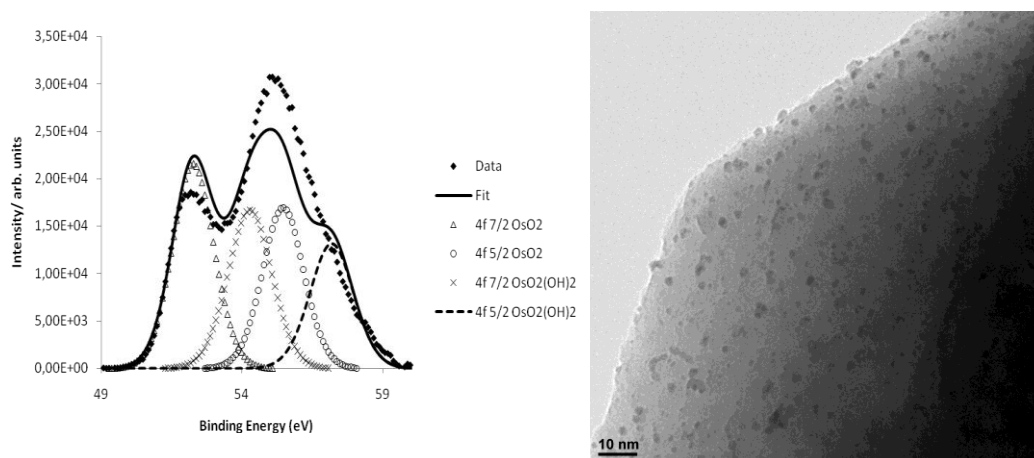


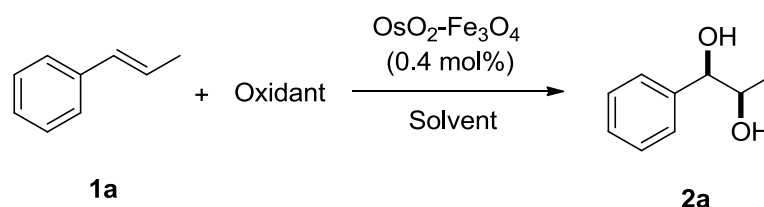
Figure 1. X-Ray photoelectron spectroscopy and TEM image of the fresh osmium impregnated magnetite catalyst.

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/ H_2O :2/1) at $70 \text{ }^\circ\text{C}$ 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 $50 \text{ }^\circ\text{C}$ the reaction took place, although it needed a longer reaction time to achieve similar yield. The increase of the temperature to $100 \text{ }^\circ\text{C}$ allowed to obtain the corresponding diol **2a** in 72% yield in only 3 hours (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: H_2O 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, H_2O_2 , 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 hour. However, increasing the amount of the oxidant to 300 mol% did not improve the previous result. Finally, the amount of catalyst was optimized (entries 14-16), finding that a good result was obtained when 0.4 mol% of osmium was added (entry 12). However, similar yield was obtained when a lower amount of osmium (0.08 mol%) was added (entry 16), but the reaction time had to be increased up to 3 hours in order to achieve the same yield (96%). In order to test the formation of toxic volatile osmium species, after performing the reaction at 100 °C and removing carefully the catalyst and the solution, the walls and the cap of pressure tube were washed with methanol and water. This washing solution was analyzed by ICP-MS, with the amount of osmium in this washing solution being lower than 0.01% of the initial charged osmium. When the reaction was repeated with only 0.04 mol% of catalyst, the yield decreased drastically (entry 17), and in this case, when the reaction was repeated increasing the reaction time to 3 h the yield kept modest (27%). In almost all cases, the only compound detected by GC-MS analysis of the crude mixture was the product **2a**, and variable amounts of starting alkene **1a**. To the best of our knowledge, the optimal conditions found for this reaction involved the use of the lowest catalyst loading ever reported, without taking in account the possible recyclability.

Table 1. Optimization of reaction conditions^a



Entry	T (°C)	Solvent	Oxidant (mol%)	Conversion (%) ^b	t (h)	Yield (%) ^c
1	70	acetone:H ₂ O (2:1)	NMO (130)	65	24	63
2	50	acetone:H ₂ O (2:1)	NMO (130)	43	48	43
3	100	acetone:H ₂ O (2:1)	NMO (130)	72	3	72
4	130	acetone:H ₂ O (2:1)	NMO (130)	71	3	71

5	100	H ₂ O	NMO (130)	10	24	0
6	100	PhMe:H ₂ O (2:1)	NMO (130)	10	24	0
7	100	PhMe	NMO (130)	45	24	40
8	100	acetone:H ₂ O (2:1)	<i>t</i> -BuOOH (130)	15	24	0
9	100	acetone:H ₂ O (2:1)	H ₂ O ₂ (130)	5	24	0
10	100	acetone:H ₂ O (2:1)	(CH ₃) ₃ N-O (130)	55	3	52
11	100	acetone:H ₂ O (2:1)	isoquinoline <i>N</i> -oxide (130)	2	24	0
12	100	acetone:H ₂ O (2:1)	NMO (200)	99	1	97
13	100	acetone:H ₂ O (2:1)	NMO (300)	90	1	89
14 ^d	100	acetone:H ₂ O (2:1)	NMO (200)	90	1	87
15 ^e	100	acetone:H ₂ O (2:1)	NMO (200)	84	1	77
16 ^f	100	acetone:H ₂ O (2:1)	NMO (200)	55 (99) ^g	1	55
						(96) ^g
17 ^h	100	acetone:H ₂ O (2:1)	NMO (200)	20 (33) ⁱ	1	12
						(27) ⁱ

^a Reactions performed using **1a** (1 mmol) in 3 mL of solvent.

^b Calculated from GC analysis of crude mixture.

^c Isolated yield.

^d Reaction performed with 0.8 mol% of catalyst.

^e Reaction performed with 0.2 mol% of catalyst.

^f Reaction performed with 0.08 mol% of catalyst.

^g The result after 3 hours of reaction appear in parenthesis.

^h Reaction performed with 0.04 mol% of catalyst.

ⁱ The result after 48 hours of reaction appear in parenthesis

The evolution of yield of compound **2a** with the time at different catalyst loadings is depicted in Figure 2. Assuming that the equation rate is simple and that the reaction conditions permit a pseudo-first order approximation for all reagents, the equation rate could be expressed as $\text{Ln } r_{0i} = \alpha \text{ Ln } [\text{catalyst}]_i + \text{constant}$.

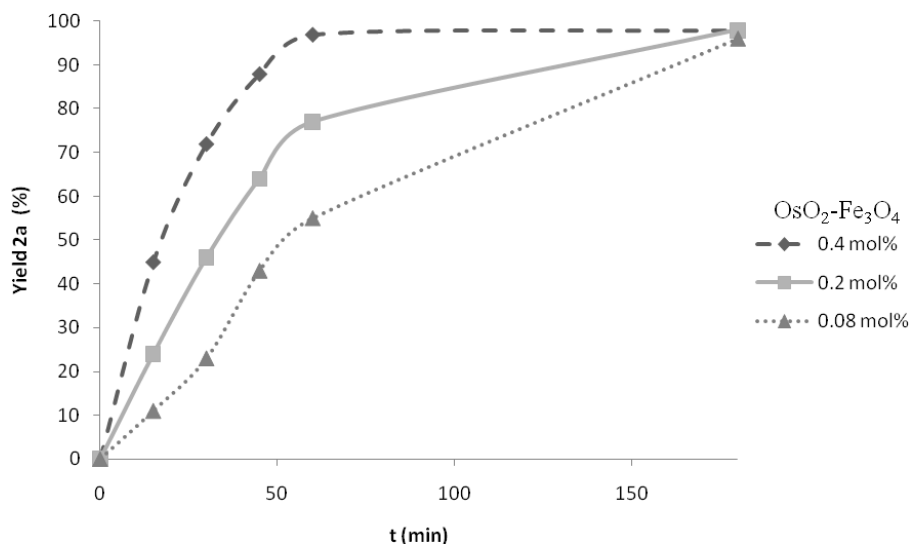


Figure 2. Plot-time yield for the standard preparation of compound **2a** using different amounts of catalyst [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

The estimation of the initial reaction rate for each trial and their representation permitted us to calculate the value of the reaction order for the catalyst (Figure 3), with the obtained value (1.1) being very close to a first order.

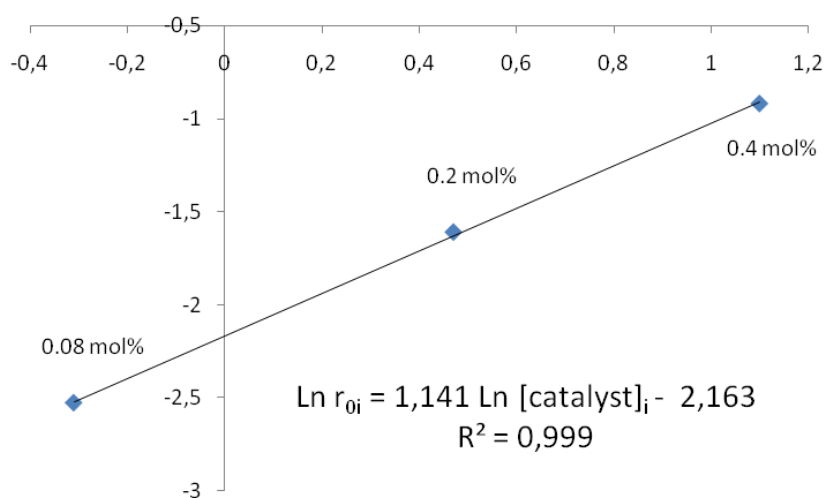


Figure 3. Correlation between initial rates and catalyst amount for the standard preparation of compound **2a** [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

The magnetite support was tested in order to confirm that it was inert, and after 24 hours the starting alkene was recovered unmodified. Other transition metal oxides impregnated on magnetite such as cobalt, nickel, copper, ruthenium, palladium, iridium, or platinum were also tested in the reaction, but none of them showed activity. Finally, the reaction was performed in absence of catalyst, and the starting material was recovered after 24 hours.

Once the activity of the catalyst was demonstrated, the problem of the recyclability was faced. After the reaction, the catalyst was kept inside the vessel using a magnet, decanting the liquid reaction media. Then, the catalyst was washed with diethyl ether, and re-used under the same reaction conditions described in the entry 16 of Table 1. Unfortunately, the yield obtained in the second cycle was only 40% after 24 hours of reaction. The ICP-MS analysis of the reaction solution, after the first trial, showed the presence of osmium (5.1% of the initial amount) and iron (0.01% of the initial amount). Meanwhile, the XRF data of used catalyst showed 1.4% of osmium amount, in good agreement with the ICP-MS analysis of reaction solution. The XPS studies showed that the iron species in the initial and in the recovered catalyst were the same. In the case of oxygen, the expected decrease of the relative intensity between oxygen bonded to osmium and to iron was also detected, being in both cases the same species (see supplementary data). However, just one species of osmium (OsO_2) on the surface of catalyst was detected (Figure 4). However, it should be pointed out that the initial catalyst data had showed the presence of OsO_2 and $\text{OsO}_2(\text{OH})_2$ in a 1:1 ratio. So, the decrease on the catalyst activity would be due to the partial leaching of the $\text{OsO}_2(\text{OH})_2$ species as well as its transformation to OsO_2 in the reaction media. Finally, it should notice that the simple removal of catalyst by a magnet is quite efficient since more than 97% of initial mass was recovered according to its weight.

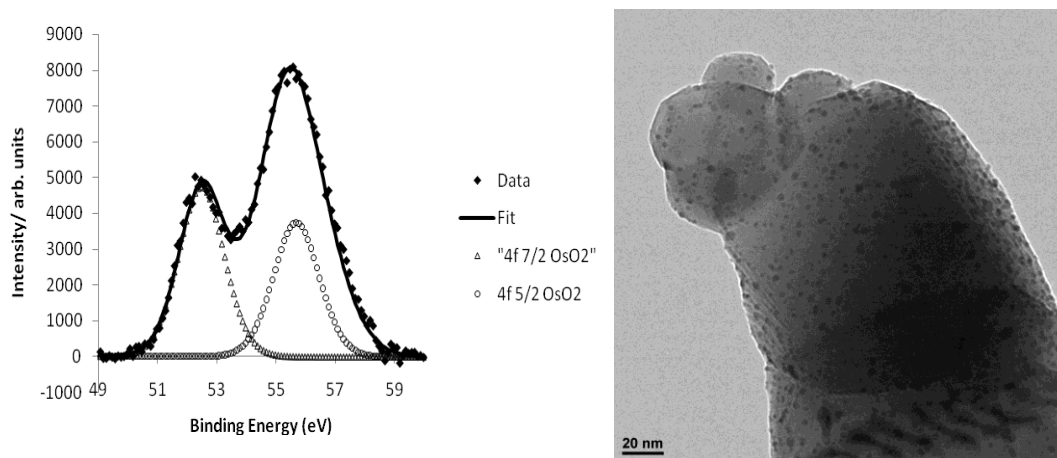


Figure 4. X-Ray photoelectron spectroscopy and TEM image of the recycled osmium impregnated magnetite catalyst [NMO (200 mol%), $\text{Me}_2\text{CO}:\text{H}_2\text{O}$ (2:1), 100 °C, 3 h].

The analysis of the TEM images of the used catalyst showed a slight process of sinterization of the particles. Initially the particles of osmium had a distribution of size of 1.7 ± 0.6 nm, and after the reaction the distribution was 2.2 ± 0.7 nm, but this change is not sufficient to explain the lost of its activity (Figure 5). The BET area of the recycled catalyst was $11.9 \text{ m}^2/\text{g}$, which is in the range of starting values.

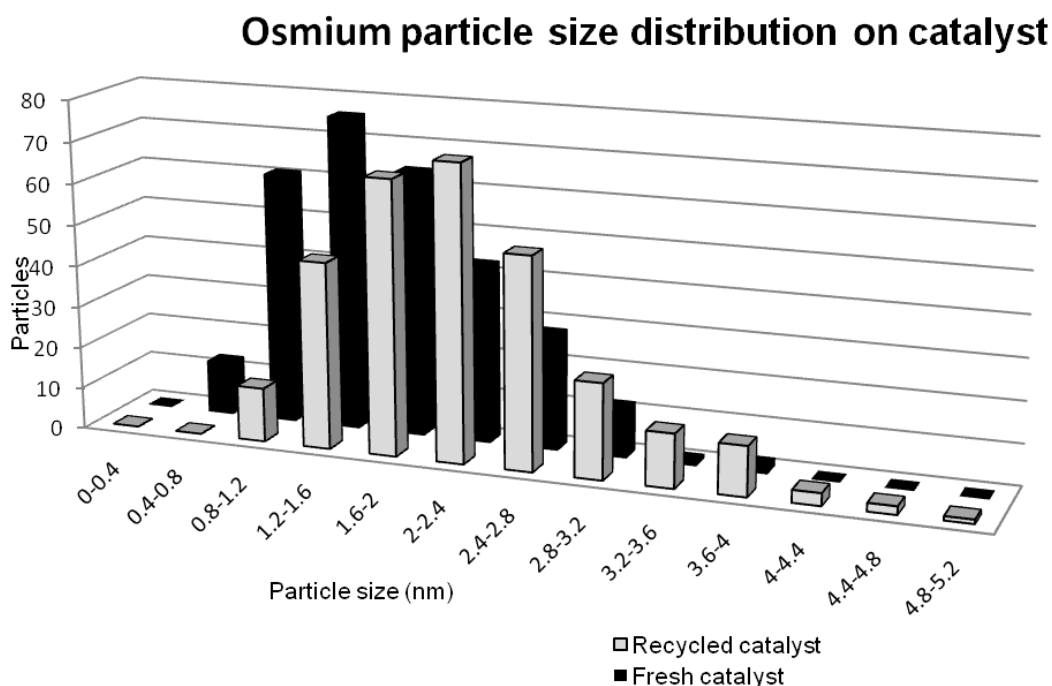
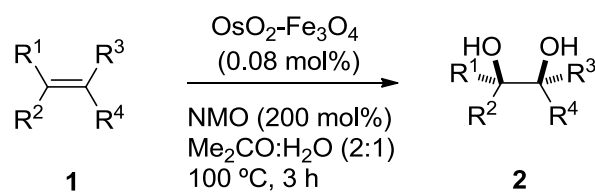


Figure 5. Particle size of fresh and recycled [NMO (200 mol%), $\text{Me}_2\text{CO}:\text{H}_2\text{O}$ (2:1), 100 °C, 3 h] osmium oxide derivatives on the surface of magnetite.

To know if the reaction took place by the leached osmium to the organic medium, we performed the standard dihydroxylation of alkene **1a** (Table 1, entry 16). After that, the catalyst was removed carefully by a magnet at high temperature. The solvents of the above solution, without catalyst, were removed under low pressure and dodec-1-ene, NMO, acetone and water were added to the above residue. The resulting mixture was heated again at 100 °C for 3 h. The analysis of crude mixture, after hydrolysis, revealed the formation of compound **2a** in 93% (catalyzed process) and product (**2j**) with only 21% yield (compare with entry 10 in Table 2). Therefore, we could not exclude that the final leached osmium was partially responsible for the reaction results.

With the best conditions in hand, the scope of the reaction was evaluated (Table 2). The reaction gave excellent yields independently of the substitution of the alkene (entries 1-5). A slight decrease in the yields was observed when 1,1-disubstituted alkenes were used (entries 4 and 5). Then, the influence of the configuration of the alkene was evaluated performing the reaction with (*Z*)- and (*E*)-stilbene (entries 6 and 7), and better result was obtained in the case of the *E*-isomer. The reaction with the *Z*-isomer rendered the expected diol in lower yield (compare entries 6 and 7), and 16% of the diol arising from the isomerization of the starting *Z*-alkene to the *E*-isomer, followed by a dihydroxylation process. However, the related aliphatic alkenes did not show this isomerization process (entries 8 and 9), and only the *syn*-dihydroxylation products were detected for the reaction of (*Z*)- and (*E*)-hex-3-ene. Excellent results were achieved when aliphatic alkenes were tested, with independence of the nature of the alkene, such as terminal or internal (entries 8-15). The tolerance of other functional groups was also tested using allylic ether or ester moieties, obtaining the corresponding diol with similar results (entries 16 and 17). Unfortunately, when the reaction was performed with a conjugated alkene, the yield decreased somewhat (entry 18), and the reaction failed when a (*Z/E*)-mixture of β -bromostyrene was used, recovering unchanged the starting material (entry 19). Finally, it should be pointed out that the selectivity of the reaction was nearly 100% since the only product detected by GC-MS from the crude mixture was the expected diol **2** and the corresponding unchanged alkene **1**, with the exception of the (*Z*)-stilbene case (entry 7).

Table 2. Dihydroxylation of alkenes^a



Entry	Alkene	Compound	Conversion (%) ^b	Yield (%) ^c
1	(<i>E</i>)-1-phenylprop-1-ene	2a	99	96
2	styrene	2b	90	87
3	1-phenylprop-1-ene	2c	99	98
4	methylenecyclopentane	2d	72	71
5	1,1-diphenylethene	2e	75	73
6	(<i>E</i>)-stilbene	2f	90	87

7	(<i>Z</i>)-stilbene	2g	75	54 ^d
8	(<i>E</i>)-hex-3-ene	2h	83	81
9	(<i>Z</i>)-hex-3-ene	2i	80	77
10	dodec-1-ene	2j	99	99
11	4-phenylbut-1-ene	2k	95	93
12	cyclohexene	2l	80	79
13	cyclooctene	2m	95	92
14	1-methylcyclohex-1-ene	2n	85	84
15	1 <i>H</i> -indene	2o	70	66
16	allyloxybenzene	2p	85	80
17	allyl benzoate	2q	90	75
18	methyl cinnamate	2r	65	49
19	(<i>Z/E</i>)- β -bromostyrene	2s	0	0 ^e

^a Reactions performed using **1** (1 mmol), NMO (2 mmol) in acetone (2 mL) and water (1 mL) at 100 °C during 3 h.

^b Calculated from GC analysis of crude mixture.

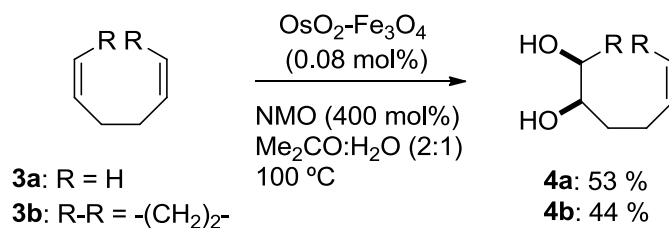
^c Isolated yield.

^d Compound **2f** was isolated in 16% yield.

^e Starting material recovered unchanged.

The same reaction conditions were applied to afford the hydroxylation of dienes (Scheme 1). However, the only isolated product from the reaction media was the diol arising from a monodihydroxylation process in low yields using 400 mol% of oxidant, with the starting reagent being the other product detected by CG-MS from the crude reaction media. The catalyst was selective for this process, because the double dihydroxylation product was not detected even when a large excess of oxidant was

added (800 mol%). It should be pointed that the reaction gave the monohydroxylation products in similar yields (**4a**: 49%, **4b**: 42%), with only 200 mol% of oxidant.



Scheme 1. Selective dihydroxylation of 1,5-dienes.

4. Conclusion

In conclusion, we have demonstrated that the impregnated osmium on magnetite system is a good catalyst for the dihydroxylation of alkenes, with one of the lowest osmium loadings described for heterogeneous catalyst so far. An interesting selectivity was achieved in the case of 1,5-dienes, with only the monodihydroxylation process being performed. Moreover, the catalyst is easily removed from the reaction medium just by the use of a simple magnet.

Acknowledgements

This work was supported by the Spanish Ministerio de Economía y Competitividad (CTQ2011-24151). J. M. P. thanks the M.E.C. for a fellowship through the FPI program. We gratefully acknowledge the polishing of our English by Mrs. Oriana C. Townley.

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Supplementary data

Physical and spectroscopic data, literature, and copies of ^1H - and ^{13}C -NMR for all compounds **2** and **4**, XPS-spectra, and TEM images are included.

Captions:

Table 1. Optimization of reaction conditions

Table 2. Dihydroxylation of alkenes

Scheme 1. Selective dihydroxylation of 1,5-dienes

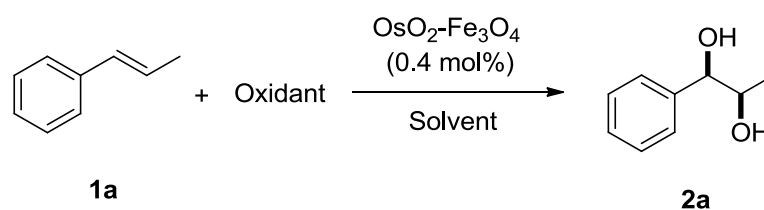
Figure 1. X-Ray photoelectron spectroscopy and TEM image of the fresh osmium impregnated magnetite catalyst.

Figure 2. Plot-time yield for the standard preparation of compound **2a** using different amounts of catalyst [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

Figure 3. Correlation between initial rates and catalyst amount for the standard preparation of compound **2a** [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

Figure 4. X-Ray photoelectron spectroscopy and TEM image of the recycled osmium impregnated magnetite catalyst [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

Figure 5. Particle size of fresh and recycled [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h] osmium oxide derivatives on the surface of magnetite.

Table 1. Optimization of reaction conditions^a

Entry	T (°C)	Solvent	Oxidant (mol%)	Conversion (%) ^b	t (h)	Yield (%) ^c
1	70	acetone:H ₂ O (2:1)	NMO (130)	65	24	63
2	50	acetone:H ₂ O (2:1)	NMO (130)	43	48	43
3	100	acetone:H ₂ O (2:1)	NMO (130)	72	3	72
4	130	acetone:H ₂ O (2:1)	NMO (130)	71	3	71
5	100	H ₂ O	NMO (130)	10	24	0
6	100	PhMe:H ₂ O (2:1)	NMO (130)	10	24	0
7	100	PhMe	NMO (130)	45	24	40
8	100	acetone:H ₂ O (2:1)	<i>t</i> -BuOOH (130)	15	24	0
9	100	acetone:H ₂ O (2:1)	H ₂ O ₂ (130)	5	24	0
10	100	acetone:H ₂ O (2:1)	(CH ₃) ₃ N-O (130)	55	3	52
11	100	acetone:H ₂ O (2:1)	isoquinoline <i>N</i> -oxide (130)	2	24	0
12	100	acetone:H ₂ O (2:1)	NMO (200)	99	1	97
13	100	acetone:H ₂ O (2:1)	NMO (300)	90	1	89
14 ^d	100	acetone:H ₂ O (2:1)	NMO (200)	90	1	87
15 ^e	100	acetone:H ₂ O (2:1)	NMO (200)	84	1	77
16 ^f	100	acetone:H ₂ O (2:1)	NMO (200)	55 (99) ^g	1	55
						(96) ^g
17 ^h	100	acetone:H ₂ O (2:1)	NMO (200)	20 (33) ⁱ	1	12

^a Reactions performed using **1a** (1 mmol) in 3 mL of solvent.

^b Calculated from GC analysis of crude mixture.

^c Isolated yield.

^d Reaction performed with 0.8 mol% of catalyst.

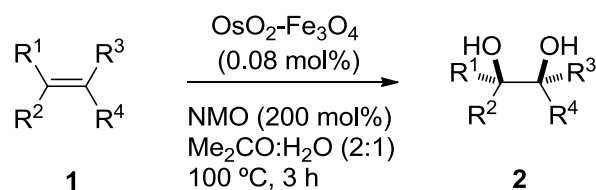
^e Reaction performed with 0.2 mol% of catalyst.

^f Reaction performed with 0.08 mol% of catalyst.

^g The result after 3 hours of reaction appear in parenthesis.

^h Reaction performed with 0.04 mol% of catalyst.

ⁱ The result after 48 hours of reaction appear in parenthesis

Table 2. Dihydroxylation of alkenes^a

Entry	Alkene	Compound	Conversion (%) ^b	Yield (%) ^c
1	(<i>E</i>)-1-phenylprop-1-ene	2a	99	96
2	styrene	2b	90	87
3	1-phenylprop-1-ene	2c	99	98
4	methylenecyclopentane	2d	72	71
5	1,1-diphenylethene	2e	75	73
6	(<i>E</i>)-stilbene	2f	90	87
7	(<i>Z</i>)-stilbene	2g	75	54 ^d
8	(<i>E</i>)-hex-3-ene	2h	83	81
9	(<i>Z</i>)-hex-3-ene	2i	80	77
10	dodec-1-ene	2j	99	99
11	4-phenylbut-1-ene	2k	95	93
12	cyclohexene	2l	80	79
13	cyclooctene	2m	95	92
14	1-methylcyclohex-1-ene	2n	85	84
15	1 <i>H</i> -indene	2o	70	66
16	allyloxybenzene	2p	85	80
17	allyl benzoate	2q	90	75
18	methyl cinnamate	2r	65	49
19	(<i>Z/E</i>)- β -bromostyrene	2s	0	0 ^e

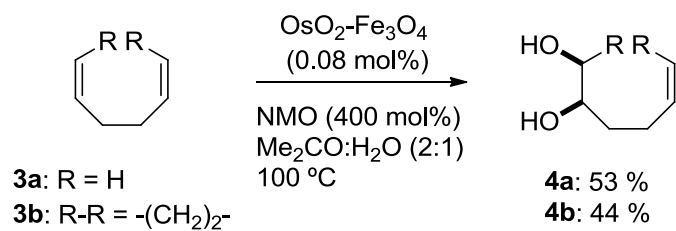
^a Reactions performed using **1** (1 mmol), NMO (2 mmol) in acetone (2 mL) and water (1 mL) at 100 °C during 3 h.

^b Calculated from GC analysis of crude mixture.

^c Isolated yield.

^d Compound **2f** was isolated in 16% yield.

^e Starting material recovered unchanged.



Scheme 1. Selective dihydroxylation of 1,5-dienes

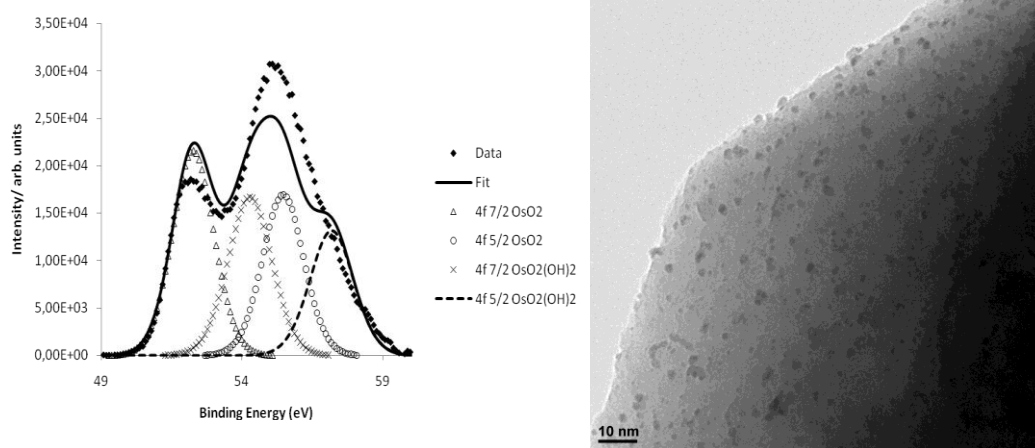


Figure 1. X-Ray photoelectron spectroscopy and TEM image of the fresh osmium impregnated magnetite catalyst.

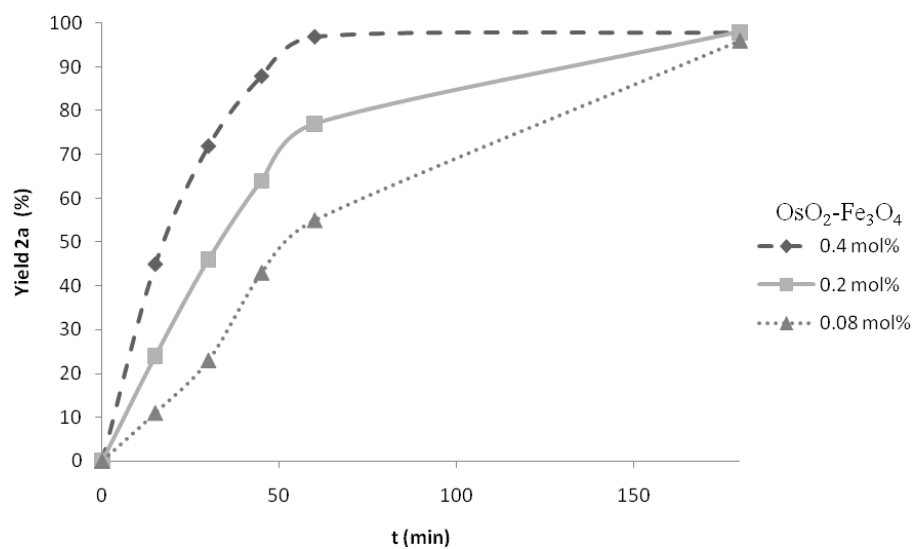


Figure 2. Plot-time yield for the standard preparation of compound **2a** using different amounts of catalyst [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

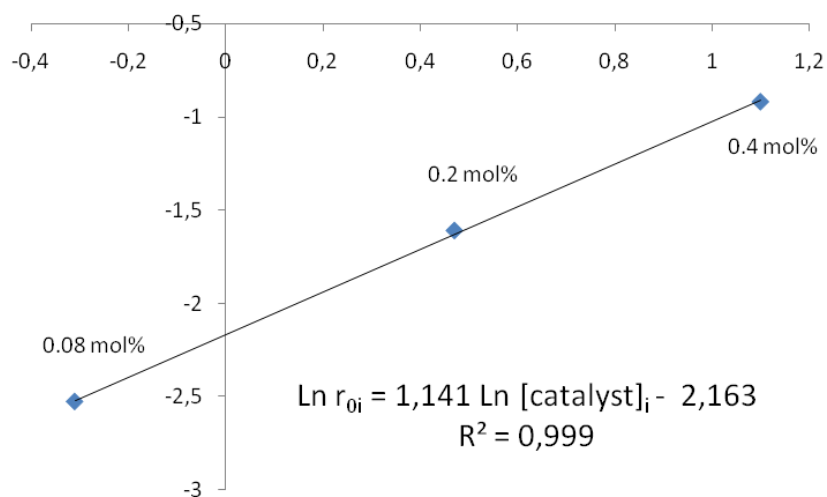


Figure 3. Correlation between initial rates and catalyst amount for the standard preparation of compound **2a** [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

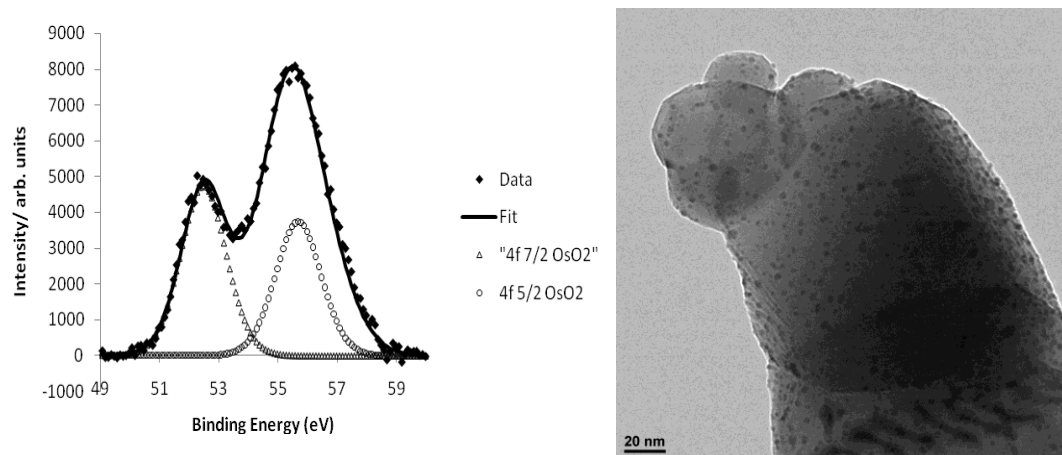


Figure 4. X-Ray photoelectron spectroscopy and TEM image of the recycled osmium impregnated magnetite catalyst [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h].

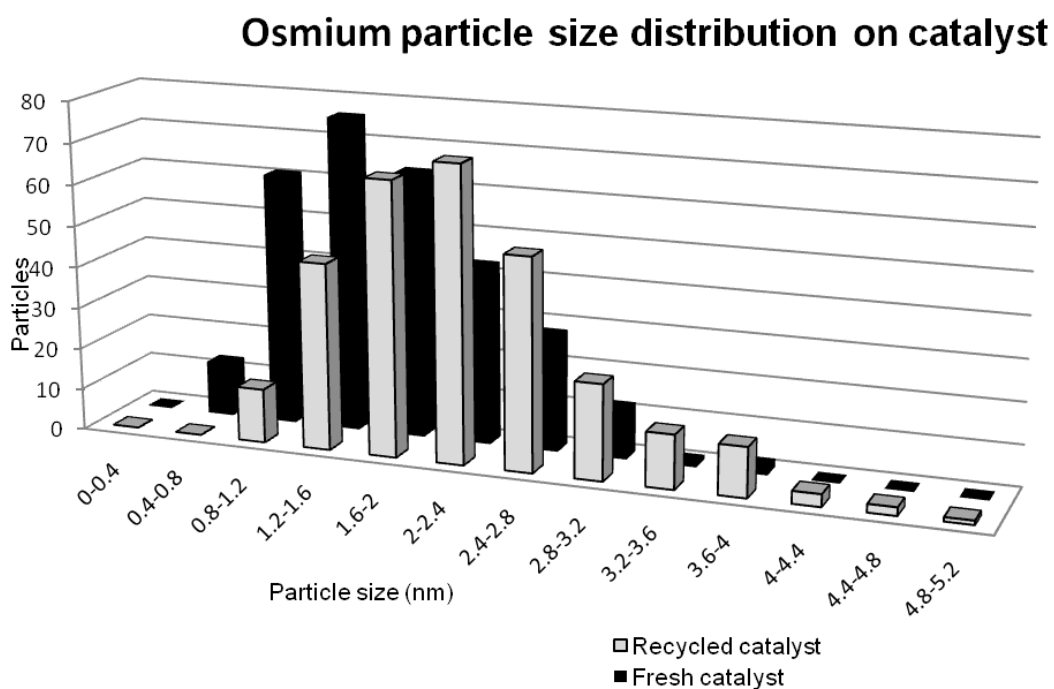


Figure 5. Particle size of fresh and recycled [NMO (200 mol%), Me₂CO:H₂O (2:1), 100 °C, 3 h] osmium oxide derivatives on the surface of magnetite.

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