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Dihydroxylation of olefins catalyzed by zeolite-confined osmium(0) nanoclusters: an efficient and reusable method for the preparation of 1,2-*cis*-diols[†]

Önder Metin,*^a Nurdan Alcan Alp,^a Serdar Akbayrak,^b Abdullah Biçer,^a Mehmet Serdar Gültekin,*^a Saim Özkar^b and Uğur Bozkaya^a

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Addressed herein is a novel, eco-friendly, recoverable, reusable and bottleable catalytic system developed for the dihydroxylation of various olefins yielding 1,2-*cis*-diols. In our protocol, zeolite-confined osmium (0) nanoclusters (zeolite-Os⁰) are used as reusable catalyst and H_2O_2 served as a co-oxidant. Zeolite-Os⁰ are found to be highly efficient and selective catalysts for the dihydroxylation of a wide range olefins in an aqueous acetone mixture at room temperature. In all of the olefins surveyed, the catalytic dihydroxylation reaction proceeds smoothly and the corresponding 1,2-*cis*-diols are obtained in excellent chemical yield under the optimized conditions. The present heterogeneous catalyst system provides many advantages, such as being eco-friendly and industrially applicable over the traditional homogenous OsO₄–NMO system for the dihydroxylation of olefins.

Introduction

The oxidation of olefins in the presence of transition metal catalysts is widely used in cyclitols chemistry for the production of important pharmaceuticals, drugs and fine chemicals.¹ Several methods have been developed for the synthesis of compounds bearing *cis*-diol group from the olefin oxidation.² Among them, the osmium catalyzed dihydroxylation of olefins is one of the most powerful synthetic protocols for the preparation of vicinal diols.³ Despite of the widespread application of this type of reaction in organic synthesis, the high cost, hazardous toxicity, volatility and contamination of products with osmium are the main drawbacks for their use in industry on the subject of green chemistry.⁴ One promising way of handling these problems is to use a heterogeneous osmium catalyst obtained by immobilization of the catalytic species on suitable inorganic or organic supports so that the recovery of the catalyst can be achieved by simple filtration of reaction mixture. As supports chiral ligands,⁵ polymers,⁶ dendrimers,⁷ iox-exchange resins,⁸ silica gels,⁹ hydroxyapatites¹⁰ and fullerenes¹¹ have been used for the immobilization of osmium catalysts. The microencapsulation¹² and miscellaneous¹³ approaches have also been reported for the

heterogenization of osmium catalysts. In all immobilization protocols used for the heterogenization of osmium catalyst so far, the osmium tetraoxide (OsO_4) was immobilized *via* molecular interaction with the support materials. However, in all cases, the immobilized OsO_4 catalyst leaches into the reaction solution as the weak molecular interaction between the support and catalyst can easily be broken, which creates problems in recovery and reusability of the catalyst.¹⁴ It is obvious that the development of a new type of heterogeneous osmium catalyst system is still needed for the dihydroxylation of olefins due to continuing problems such as the lower activity and complete recovery of the immobilized catalysts from the reaction medium.

Transition metal nanoclusters are highly active catalysts as they have large surface areas, providing a high density of active sites. They have attracted much attention in organic synthesis due to their distinct catalytic activities for various transformations.¹⁵ However, one of the most important problems in their catalytic applications is the aggregation of nanoclusters into clumps and ultimately to the bulk metal, despite using the best stabilizers,¹⁶ which leads to a vital decrease in their catalytic activity and lifetime. One of the most promising ways to prevent the aggregation is the generation of metal nanoclusters in the void spaces of mesoporous and microporous solids.¹⁷ Zeolite-Y, a FAU-type zeolite, is considered to be a suitable host providing highly ordered large cavities with an inner diameter of 1.3 nm,¹⁸ and can be used for the assembly of metal and metal oxide nanoclusters as the pore size could limit the growth of particles.¹⁹ Recently, we reported that zeolite-confined osmium(0) nanoclusters, hereafter referred to as zeolite-Os⁰, are highly active and selective catalysts in the aerobic oxidation of alcohols under mild conditions.²⁰ In addition to their activity and

^aDepartment of Chemistry, Faculty of Science, Atatürk University, 25240 Erzurum, Turkey. E-mail: ometin@atauni.edu.tr, gultekin@atauni.edu.tr ^bDepartment of Chemistry, Middle East technical University, 06800 Ankara, Turkey

[†] Electronic supplementary information (ESI) available: Copy of ¹H-NMR and ¹³C-NMR spectra and spectral data for all *cis*-diols. The details of theoretical molecular volume computations using density functional theory. Additional characterization data for the catalyst. See DOI: 10.1039/c2gc16616j

selectivity, zeolite-Os⁰ are isolable, reusable and bottleable, which are very important criteria for their application in many heterogeneous catalytic system on the subject of green chemistry. Herein we report the use of zeolite-Os⁰ as catalysts in the dihydroxylation of various olefins yielding 1,2-cis-diols in aqueous acetone at room temperature. The zeolite-Os⁰ are highly efficient and selective catalyst providing excellent yield to 1,2-cis-diols as well as eco-friendly, recoverable, reusable and bottleable catalytic system for the dihydroxylation of olefins. The catalytic dihydroxylation of olefins was performed in the presence of hydrogen peroxide as a co-oxidant in aqueous acetone at room temperature. After reaction, the solid catalyst materials were separated from the reaction solution by centrifugation easily, which is one of the major problems of the traditional OsO₄/NMO catalyst system used for the dihydroxylation of olefins. The conversion of the starting olefins to the corresponding 1,2-cis-diols was monitored by ¹H-NMR and ¹³C-NMR spectra of supernatant solution. The solid zeolite-Os⁰ catalyst recovered by centrifugation can be bottled and stored under ambient conditions. The reusability experiments performed on different types of olefin dihydroxylation revealed that zeolite-Os⁰ catalyst can be reused efficiently and preserve its initial activity with minimal loss up to 5 catalytic cycles.

Experimental

General remarks

Osmium(III) chloride trihydrate (OsCl₃·3H₂O), sodium borohydride (NaBH₄, 98%), zeolite-Y (Na₅₆[(AlO₂)₅₆(SiO₂)₁₄₀][.] 250H₂O) and all organic compounds were purchased from Sigma-Aldrich[®] and were used without further purification. Deionized water was distilled by water purification system (Milli-Q system). The osmium content of zeolite-Os⁰ samples was determined by inductively coupled plasma optical emission spectroscopy, ICP-OES (Leeman Labs.). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C. Transmission electron microscope images were obtained by a JEOL 2100 TEM (200 kV). ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian 200 MHz or Bruker Avance DPX 400 MHz spectrometer.

General procedure for the preparation of zeolite-confined osmium(0) nanoclusters

The zeolite-Os⁰ were prepared by our established procedure reported elsewhere.²⁰ In a typical procedure, osmium(III) cations were introduced into the zeolite-Y by ion exchange of 1.0 g zeolite-Y in 100.0 mL aqueous solution of 77.0 mg OsCl₃·3H₂O for 72 h at room temperature. The opaque-brown supernatant solution became colorless after 72 h, indicating complete ion exchange. Next, the sample was filtered by suction filtration, washed three times with 20 mL of deionized water and dried under vacuum at room temperature. Osmium content of the Os³⁺-exchanged zeolite-Y sample was found as 2.1 wt% by ICP-OES analysis corresponding to 64% of osmium used for the ion exchange (Os_{2.5}Na_{48.5}[(AlO₂)₅₆(SiO₂)₁₄₀]·250H₂O). Then, 0.4 g Os³⁺-exchanged zeolite-Y was added into 100.0 mL of

150 mM NaBH₄ solution at room temperature. The solid powders were isolated again by suction filtration when the hydrogen generation from the reaction solution ended (~3 h), washed three times with 20.0 mL of deionized water to remove metaborate and chloride anions and were dried under vacuum at ambient temperature. The samples of zeolite-Os⁰ were bottled as black powders.

General procedure for the *cis*-dihydroxylation of olefins catalyzed by zeolite-confined osmium(0) nanoclusters

In a typical procedure, 2.0 mmol of a selected olefin was transferred into a single-necked flask and then 10.0 mL of aqueous acetone (acetone/H₂O = 9 : 1 v/v) was added into the alkene solution at room temperature. The resulting mixture was vigorously stirred until a homogenous mixture obtained, while 0.18 mL of H₂O₂ (1 equiv to alkene) was gradually added by syringe. Next, 100.0 mg of dried zeolite-Os⁰ catalyst was added into the reaction mixture and was stirred vigorously to obtain a well dispersed mixture, which was stirred at room temperature for 24 hours. Next, another 0.18 mL of H₂O₂ was gradually added by syringe into the reaction mixture after 24 hours. The resulting mixture was stirred for a further 24 hours at room temperature. At the end of the 48 hours, the reaction mixture was centrifuged at 6000 rpm for 10 min. The supernatant of the centrifuged sample was transferred into a glass vial containing NaHSO3 and was agitated for 5 min to remove excess H₂O₂. Hereafter, the resulting heterogeneous mixture was isolated via suction filtration, the aqueous acetone was removed on a rotary evaporator. The desired *cis*-diols were obtained in good yields. The precipitate (zeolite-Os⁰ catalyst) was washed with 20.0 mL of acetone 2 times to remove residues and was bottled for re-use. A copy of the ¹H-NMR and ¹³C-NMR spectra and spectral data are given in ESI.†

General procedure for acetylation of 1,2-cis-diols

All the *cis*-diols were also characterized after their transformation into corresponding acetates. The *cis*-diols were dissolved in 20.0 mL of methylene chloride and then 2.0 mL of pyridine and 2.5 equiv of acetic anhydrate were added into the solution. The resulting mixture was stirred over night (approximately 12 h) at room temperature. Next, the solution was poured into icy HCI (20.0 mL of 2.0 N) and stirred for 5 min. The solution was extracted with ethyl acetate (3×30 mL) and the ethyl acetate phases were collected in a glass bottle and were then washed with saturated NaHCO₃ solution (2×30 mL). Next, the resulting solution was washed with water to remove the inorganic impurities. Finally, the organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated in a vacuum, the crude products were purified by silica-gel column chromatography. The acetylated products were obtained in high chemical yields (68–83%).

Computational methods

For each molecule considered in this research, theoretical molecular volume computations were carried out using a Gaussian 03 program package.²¹ Density functional theory (DFT) was employed for this purpose. Geometry optimizations, harmonic vibrational frequencies, molecular volumes are computed with the B3LYP functional.^{22,23} In all computations Pople's polarized double- ζ split valence basis set, 6-31G(d), is employed.^{24–26}

Results and discussion

Traditional cis-dihydroxylations of olefins are generally performed in the presence of osmium tetraoxide (OsO₄) as a homogeneous catalyst and N-methyl-morpholine oxide (NMO) as a co-oxidant in various hazardous organic solvents, such as toluene and tetrahydrofurane.^{3b} Besides the traditional OsO₄-NMO method, an alternative route including ruthenium(III) chloride (RuCl₃) as a homogeneous catalyst, sodium periodide (NaIO₄) as a co-oxidant and H₂SO₄ as a solvent was used in the dihydroxylation of olefins.²⁷ Many hazardous chemicals and irreversible homogenous catalyst systems are used in all protocols mentioned above. Moreover, the use of OsO₄ and RuCl₃ as homogeneous catalysts in the olefin dihydroxylation reactions is not practical due to their high costs. In this regard, we report herein a novel, practical, eco-friendly and industrially applicable method for the synthesis of various 1,2-cis-diols via dihydroxylation of olefins in the presence of zeolite-Os⁰ and hydrogen peroxide. In our protocol, zeolite-Os⁰ is used as a reusable heterogeneous catalyst and H₂O₂ serves as an environmentally benign co-oxidant. All catalytic olefin dihydroxylation reactions are performed in aqueous acetone at room temperature.

The zeolite-Os⁰ catalyst was prepared by the ion-exchange of Os³⁺ ions with the extra framework Na⁺ ions of zeolite-Y followed by reduction of the Os³⁺ ions in solution according to our reported procedure and well-characterized by using various advanced techniques.²⁰ The osmium content of zeolite-Os⁰ was determined as 2.1 wt% Os by inductively coupled plasma optical emission spectroscopy (ICP-OES) and all osmium loadings in the catalytic olefin dihydroxylation reactions were calculated according to the ICP-OES results. Zeolite-Os⁰ was found to be a highly efficient and selective catalyst for the dihydroxylation of a wide range of olefins. In all of the olefins surveyed, the catalytic dihydroxylation reaction proceeds smoothly and the corresponding 1,2-cis-diols are obtained in excellent chemical yield under the optimized conditions (Table 1, entries 1–12). For instance, the dihydroxylation of styrene (1a) gives styrene-cisdiol (1b) in 98% chemical yield under the optimized conditions (Table 1, entry 1). Our catalysis protocol can also be applied to other families of olefins including α , β -unsaturated cyclic carbonyl systems with or without different -R groups, which have a large tendency to undergo 1,4-conjugate additions. For example, the dihydroxylation of cyclopentenone (8a) and cyclohexzenone (9a) were converted to corresponding cis-diols (8b) and (9b), respectively, with an excellent chemical yield of 98% (Table 1, entries 8 and 9). The dihydroxylation of cyclopentenone (8a) was also performed by using traditional dihydroxylation method including OsO4-NMO system but no desired 1,2-cis-diol product was obtained even by repeating catalytic experiments several times. Dihydroxylation of other olefins were examined by using the zeolite-Os⁰ catalysis protocol, and the results depicted in Table 1. It is worth mentioning that our catalyst showed better performance in terms of chemical yields of the

Table 1 *cis*-Dihydroxylation of various olefins catalyzed by zeolite- Os^0 in the presence of H_2O_2 as a co-oxidant^{*a*}



Entry	Olefin (a)	Product (b)	Time (h)	Yield ^b (%)	TON/ TOF ^c
1	Ph	но ОН	70	98	196/2.8
2	Ph	HO OH Ph	96	98	196/2.1
3	Ph	Ph OH Ph	96	30	60/0.6
4	\square	но	48	70	140/2.9
5	\bigcirc	HOHO	52	87	174/3.4
6	\bigcirc	но	65	86	172/2.6
7	\bigcirc	HOHO	70	90	180/2.6
8	Ď	HO	55	98	196/3.6
9		но	35	98	196/5.6
10			65	98	196/3.0
11			96	25	50/0.5
12	Ph	HO HO HO	96	25	50/0.5

Turn over frequency (TOF, h^{-1}) = TON/time.^{*a*} All reactions were performed in aqueous acetone (20.0 mL, acetone/water = 9:1 v/v) using zeolite-Os⁰ catalyst (100.0 mg, 2.1 wt% Os), olefin (2 mmol), H₂O₂ (2 equiv) at room temperature. All the *cis*-diols were also characterized after their transformation into corresponding acetates. ^{*b*} Isolated yield. ^{*c*} Turn over number (TON) = moles of substrate converted per mole of Os.

product and TON values as compared to the mesoporous^{28a} or mesoporous–transition metal hybrid materials^{28b} tested as catalysts in the dihydroxylation of olefins under similar reaction conditions.

To examine the effect of temperature on our protocol, we have performed the catalytic dihydroxylation of (1a), (7a) and (9a) at different temperatures (35 and 50 °C) under the optimized conditions. The ¹H-NMR spectra of the products obtained by catalytic dihydroxylation of olefins at different temperature (see ESI⁺) showed that the higher oxidation of olefins took place and corresponding aldehydes were formed as by-products at higher reaction temperatures. Additionally, the ratio of corresponding aldehydes to desired product of 1,2-cis-diols increases by increasing reaction temperature. For example, the dihydroxylation of cyclooctene (Table 1, entry 7) gives the corresponding aldehydes and 1,2-cis-diol with an integration ratio of 3/7 (aldehyde/1,2-cis-diol) at 35 °C and the ratio increases to 1/1 at 50 °C. We can conclude by these results that the selectivity of our catalyst decreases by increasing temperature while it works well at room temperature, which is more important for green chemistry applications.

It is noteworthy to discuss the intriguing results obtained by catalytic dihydroxylation of *trans*-stilbene (**2a**) and *cis*-stilbene (**3a**). The dihydroxylation of (**2a**) gives the major product (**2b**), 1,2-*trans*-diphenyl ethane-1,2-*cis*-diol, in a very high chemical yield of 98% (Table 1, entry 2), while that of (**3a**) results in the formation of the corresponding 1,2-*cis*-diol (**3b**) in a lower chemical yield of 30% under the optimized reaction conditions (Table 1, entry 3). Actually, this result provides compelling evidence for the formation of osmium(0) nanoclusters mostly within the cages of zeolite-Y, which has an aperture diameter of 7.4 Å.¹⁸ Additionally, the HRTEM image of zeolite-Os⁰ (see ESI, Fig. S1[†]) also shows the osmium(0) nanoclusters within the cages of zeolite-Y.

Theoretical molecular volume computations using density functional theory (DFT) was also carried on molecules (2a), (3a), (10a), (11a) and (12a) for calculation of their Lennard-Jones kinetic diameters to discuss their availability to enter into zeolite cages, where the catalytic reaction takes place. Details of the theoretical study performed on the molecules to calculate their Lennard-Jones kinetic diameters can be seen in ESI.† The Lennard-Jones kinetic diameter of trans-stilbene (2a) is calculated as 7.1 Å, which permits its entrance into cages of zeolite-Y, while that of *cis*-stilbene (3a) is large (7.8 Å), which does not permit its entrance into the cages of zeolite-Y. Additionally, the low yield dihydroxylation of cis-stilbene (3a) indicates the existence of some osmium(0) nanoclusters on the external surface of zeolite-Y, which are available for the large substrate molecules as well. The transmission electron microscopy (TEM) image (Fig. 1) confirms the existence of osmium(0) nanoclusters on the external surface of zeolite as well as some in the cavities. Similar results were also obtained for the catalytic dihydroxylation of cyclohexene derivatives (10a) and (11a). Cyclohex-2-en-1-yl acetate (10a) has one acetate group perpendicular to plane, while cyclohex-2-en-1,4-diacetate (11a) has two acetate groups in 1,4 position. The theoretical calculations showed that compound (11a) has a Lennard-Jones kinetic diameter of 7.6 Å, which is large for its entrance into the cages of zeolite-Y, while that of compound (10a) is 6.9 Å, which permits its entrance into

the cages of zeolite-Y. A similar theoretical explanation was also valid for the low yield dihydroxylation of cyclohex-2-en-1-ylbenzoate (**12a**) having calculated the Lennard–Jones kinetic diameter of 7.9 Å. In light of the theoretical study results, it can be concluded that the present catalytic dihydroxylation method is not applicable for the molecules having a Lennard–Jones kinetic diameter larger than the aperture size of the zeolite-Y cages (7.4 Å).

The zeolite- Os^0 catalyst was recovered from the reaction solution by simple centrifugation and re-used in the dihydroxylation of various olefins (Table 2, entries 1–5). The recovered zeolite- Os^0 catalysts preserve their initial activity even after 5th catalytic runs without any important loss in the chemical yield (the decrease in the chemical yields is in the range of 3–7%). of dihydroxylation of selected alkenes to corresponding 1,2-*cis*-diols



Fig. 1 TEM image of osmium(0) nanoclusters formed on the external surface of zeolite-Y.

Table 2 Reusability of zeolite- Os^0 catalyst in the dihydroxylation of various olefins^{*a*}

Entry	Olefin (a)	Product (b)	Yield (%) 1st run	Yield (%) 5th run
1	Ph	НО ОН	98	95
2	Ph	HO OH Ph	98	91
3	Ph	Ph [*]	90	85
4			98	92
5			98	91

^{*a*} All reactions were performed in aqueous acetone (20.0 mL, acetone– water = 9:1 v/v) using 100.0 mg zeolite-Os⁰ (2.1 wt% Os), 2 mmol olefin (5 times), 2 equiv H₂O₂ (5 times) at room temperature.

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(Table 2, entries 1–5). The decrease in the isolated yields of *cis*diols over the reusability test most probably stems from the loss of some of the zeolite- Os^0 catalyst during the centrifugation and drying process. The ICP-OES analyses performed on the supernatant of the catalytic reaction solutions revealed that a negligible amount of osmium was detected (<1 ppm), which is clear evidence of no leaching of the osmium into the reaction solution.

Conclusions

In conclusion, we have developed a facile recoverable, reusable and bottleable catalyst system for the dihydroxylation of olefins to 1,2-*cis*-diols. Zeolite-confined osmium(0) nanoclusters exhibited excellent activity in the olefin dihydroxylation. The present heterogeneous catalyst system is novel and provides many advantages such as being eco-friendly and industrially applicable over the homogenous one for the dihydroxylation of olefins. We hope that the method described here might open a new perspective for the application of heterogeneous catalysts in the dihydroxylation of olefins for the synthesis of many important compounds bearing diol groups in the context of green chemistry.

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