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Catalytic Asymmetric Dihydroxylation of Olefins with Reusable OsO_4^{2-} on Ion-Exchangers: The Scope and Reactivity Using Various Cooxidants

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Abstract: Exchanger-OsO_4 catalysts are prepared by an ion-exchange technique using layered double hydroxides and quaternary ammonium salts covalently bound to resin and silica as ion-exchangers. The ion-exchangers with different characteristics and opposite ion selectivities are specially chosen to produce the best heterogeneous catalyst that can operate using the various cooxidants in the asymmetric dihydroxylation reaction. LDH-OsO_4 catalysts composed of different compositions are evaluated for the asymmetric dihydroxylation of *trans*-stilbene. Resin-OsO_4 and SiO_2-OsO_4 designed to overcome the problems associated with LDH-OsO_4 indeed show consistent activity and enantioselectivity in asymmetric dihydroxylation of olefins using $K_3Fe(CN)_6$ and molecular oxygen as cooxidants. Compared to the Kobayashi heterogeneous systems, resin-OsO_4 is a very efficient catalyst for the dihydroxylation of a wide variety of aromatic, aliphatic, acyclic, cyclic, mono-, di-, and trisubstituted olefins to afford chiral vicinal diols with high yields and enantioselectivities irrespective of the cooxidant used. Resin-OsO_4 is recovered quantitatively by a simple filtration and reused for a number of cycles with consistent activity. The high binding ability of the heterogeneous osmium catalyst enables the use of an equimolar ratio of ligand to osmium to give excellent enantioselectives in asymmetric dihydroxylation in contrast to the homogeneous osmium system in which excess molar quantities of the expensive chiral ligand to osmium are invariably used. The complexation of the chiral ligand $(DHQD)_2PHAL$, having very large dimension, a prerequisite to obtain higher ee, is possible only with the OsO_4^{2-} located on the surface of the supports.

Introduction

The increasing demand of chemical and pharmaceutical industries for enantiomerically pure compounds has prompted the development of several chirotechnologies, which aim to exert the ultimate control over a chemical reaction by directing its enantioselectivity. Heterogeneous enantioselective catalysis is particularly attractive because it allows production and ready separation of large quantities of chiral product while using a small amount of catalyst. The Sharpless catalytic asymmetric dihydroxylation (AD) of olefins, an inspiring invention, provides one of the most elegant methods for the preparation of chiral vicinal diols.[1,2] Although the AD reaction offers a number of processes that could be applied to the synthesis of pharmaceuticals, fine chemicals, etc., the high cost, toxicity, and possible contamination of osmium catalysts in the products restrict its use in industry. Heterogenization of the ligands on soluble and insoluble polymers[3−5] or silica gel[6] support and eventual complexation with osmium, a possible solution to address this issue attempted by several groups, does not allow one to recover and reuse osmium, as the affinity of anchored ligands for osmium tetroxide is weak.

The microencapsulation technique adopted by Kobayashi to envelop OsO_4 in a polymer capsule affords a recoverable and reusable osmium catalyst for the AD reaction.[7] In another fascinating design, OsO_4 was immobilized onto a silica anchored

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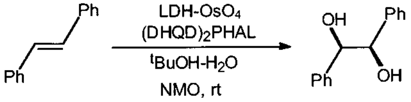
tetrasubstituted olefin by Jacobs, but its application is limited to achiral dihydroxylations due to formation of the diol via a bisglycolate intermediate.[8]

Various cooxidants such as *N*-methylmorpholine *N*-oxide (NMO),[9] $K_3Fe(CN)_6$,[10] and very recently molecular oxygen[11] are effectively used to facilitate the Os(VI)/Os(VIII) catalytic cycle that allows the use of catalytic amounts of osmium tetra oxide in the dihydroxylation reaction. Each of the cooxidants used has its own advantages and disadvantages. $K_3Fe(CN)_6$ is a very effective cooxidant in the osmium-catalyzed dihydroxylation of various classes of olefins composed of aromatic, aliphatic, cyclic, acyclic, mono-, di-, tri-, and tetrasubstituted olefins affording chiral diols in high yield and very high enantioselectivity. However, the use of potassium ferricyanide in the AD reaction has certain drawbacks that include handling of large amounts of salts (1.4 g per mmol of olefin) and effluent disposal. Therefore, the ferricyanide cooxidant is not feasible practically or economically on a large scale. The use of NMO has definite advantages:[9] unlike the iron byproduct formed in the usual reaction, the reduced byproduct from NMO, *N*-methylmorpholine (NMM), is easily removed and recycled if necessary. Second, NMO is economical, by a factor of 5 when compared to the amount of ferricyanide/carbonate salts required per mole of olefin. Third, the NMO-based reactions can be run in high concentrations (2 M), while the concentration of ferricyanide-based reactions is limited by the solubility of the salts. By adopting slow addition of olefin to the reaction mixture with the aid of an automated pump, the aromatic olefins give ee's as high as those obtained with the $K_3Fe(CN)_6$ cooxidant. An interesting development was made by Backvall et al. in realizing the higher economical process by using H_2O_2, the stoichiometric oxidant, and NMM in catalytic amounts to continuously generate NMO in situ via oxidation of the latter using biomimic flavin[12a,b] or vanadyl acetylacetonate[12c] as the electron-transfer mediator in a multicomponent catalytic system for the AD reaction of olefins. Recently, we demonstrated the reoxidation of NMM to facilitate continuous in situ production of NMO to sustain the Os(VI)/Os(VIII) catalytic cycle induced by a bifunctional heterogeneous catalyst composed of osmium and tungsten oxides on the single matrix using H_2O_2 as the terminal oxidant.[13b] Both of the methodologies are very cost-effective. However, dispensing the use of $K_3Fe(CN)_6$ with NMO altogether is not possible, as the NMO gives inferior ee's in the case of aliphatic olefins. Recently, the Krief and Beller groups reported the most economical and promising protocol for the osmium-catalyzed AD of olefins using molecular oxygen or air as the cooxidant.[11] Although molecular oxygen is believed to be the most economical and environmentally acceptable cooxidant in the AD reaction, the lower yields and ee's and limited scope of utility are its disadvantages. The overoxidation of diols containing α-hydrogen at benzylic positions to carbonyl compounds during the AD reaction of aromatic olefins using oxygen as the cooxidant lowers the chemoselectivities of the reaction as compared to that with aliphatic olefins. The basic pH media required for the AD reaction while using oxygen as cooxidant effects the hydrolysis of esters and thus precludes the use of olefins containing ester functions. It is, therefore, an incentive to develop a heterogeneous catalyst that performs AD reactions with higher yields and enantioselectivities using NMO, $K_3Fe(CN)_6$, or molecular oxygen as a cooxidant.

Scheme 1. Dihydroxylation of *trans*-Stilbene



Recently, we designed and developed an ion-exchange technique for a recoverable and reusable osmium catalyst immobilized on layered double hydroxides (LDH) by the ion-exchange of OsO_4^{2-} for AD of olefins employing NMO as the cooxidant (Scheme 1).[13a] Although the LDH-OsO_4 shows excellent activity with NMO, it is deactivated when $K_3Fe(CN)_6$ or molecular oxygen is used as a cooxidant. Therefore, we felt it is necessary to develop a robust catalytic system to withstand vagaries of the reaction conditions induced by various cooxidants. We herein describe the results of a detailed investigation undertaken on specially designed exchanger-OsO_4 catalysts comprising LDH with different compositions and quaternary ammonium salts covalently bound to resin and silica as ion-exchangers for the AD of olefins using the cooxidants NMO, $K_3Fe(CN)_6$, or molecular oxygen in an effort to understand the reactivity, versatility, and robustness of the catalytic systems. Incidentally, this forms the first report of a heterogeneous osmium-catalyst-mediated AD reaction of olefins using molecular oxygen as the cooxidant.

Results and Discussion

Preparation of Exchanger-OsO_4. To understand the scope and generality of the ion-exchange technique for immobilization of OsO_4, various ion-exchangers sourced from inorganic[14,15] and organic materials[16] were prepared (Scheme 2) and examined in dihydroxylation reactions using various cooxidants. The ion-

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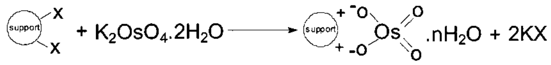
Scheme 2. Synthesis of Exchanger-OsO_4 Catalysts



exchange materials with opposite exchange properties were deliberately chosen to immobilize OsO_4^{2-} to evolve the best catalyst that withstands the vagaries of the reaction conditions in the AD of olefins induced by the use of different cooxidants. LDH is a class of layered material consisting of alternating cationic $M(II)_{1-x}M(III)_x(OH)_2^{x+}$ and anionic $A^{n-}\cdot zH_2O$ layers.[17] The cationic layers are separated from each other by anions and water molecules. The positively charged layers in LDH contain edge-shared metal M(II) and M(III) hydroxide octahedra, with charges neutralized by A^{n-} anions located in the interlayer spacing or at the edges of the lamellae. LDH containing various divalent and trivalent cations [M(II) = Mg, Zn, Ni, Cu; M(III) = Al, Ga, In, Cr, Fe] in combination with different anions can be prepared. LDH have extensively been investigated in a wide range of applications such as catalysts,[18] adsorbents,[17,19] ceramic precursors,[20] reaction media for controlled photochemical[21] and electrochemical reactions,[22] and bioactive nanocomposites.[23] Small hexagonal LDH crystals with $Mg_{1-x}Al_x(OH)_2(A)_x\cdot zH_2O$ [A = Cl, NO_3, CO_3] composition were synthesized following existing procedures.[17b] OsO_4^{2-} was exchanged onto the chloride-saturated LDH to obtain LDH-OsO_4. Resins are another class of polymeric supports originating from organic precursors, which are widely employed as catalyst carriers and also in solid-phase organic synthesis. Silica gel, an inorganic support that is commonly employed in heterogeneous catalysis, is also considered for the immobilization of osmium. Similarly, OsO_4^{2-} was also exchanged onto quaternary ammonium groups covalently bound to modified silica and organic resin to obtain SiO_2-OsO_4 and resin-OsO_4.

Characterization of Catalysts. All of these catalysts were well characterized[13a] by IR, UV-DRS, SEM, and XPS. The FTIR spectra of these catalysts show a broad absorption band near 800−855 cm^{-1} which is assigned to the vibrational asymmetric O=Os=O stretching unlike a sharp band observed at 819 cm^{-1} in the potassium osmate spectrum. The broad bands observed almost in the same region with the different exchanger-OsO_4 catalysts indicates that the osmate is unchanged upon exchange onto the support except for experiencing very weak interactions with the support. The diffuse reflectance UV/vis spectra of the exchanger-OsO_4 catalysts show an identical pattern to that of potassium osmate dihydrate with the absorption maxima in the range of 290−320 nm which indicates that the octahedral coordination of osmium(VI) composed of two water molecules is unperturbed upon exchange. The synthesized osmium catalysts were also characterized by X-ray photoelectron spectroscopy (XPS), and the observed Os $4f_{7/2}$ line at ~53 eV confirms that osmium is in the +VI oxidation state. Scanning electron micrographs were recorded for the samples of exchangers and exchanger-OsO_4 catalysts. The SEM studies reveal that the structure of the exchanger is unperturbed upon ion-exchange. The agglomerated flat crystallites were found in LDH-OsO_4. The resin-OsO_4 is in the form of discrete spherical beads millimeter dimension, with a distribution of sizes similar to that of the starting polymeric beads. The SEM-EDX (scanning electron microscopy-energy-dispersive X-ray analysis) of LDH-OsO_4, resin-OsO_4, and SiO_2-OsO_4 shows the presence of 18.54, 12.19, and 6.02% osmium in the respective samples. These results were revalidated by quantitative estimation of the potassium halide formed in the ion-exchange process using 0.1 N silver nitrate solution as titrant in the presence of potassium chromate. The BET surface area of LDH-OsO_4, resin-OsO_4, and SiO_2-OsO_4 is found to be 67, 8, and 317 $m^2\ g^{-1}$, respectively. X-ray powder diffraction patterns of the initial LDH and the LDH-OsO_4 hardly differ in the range $2\theta = 3°-65°$. The observed d_{003} basal spacing of the support that appeared at ~7.8 Å remains unchanged after the anion exchange, which indicates that OsO_4^{2-} is mainly located in edge positions. The possible structures for the catalysts are depicted in Figure 1.

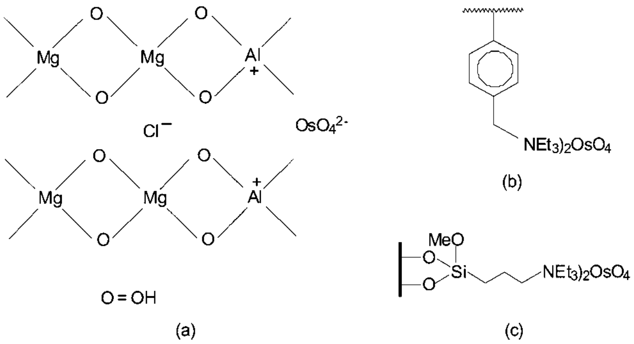


Figure 1. The structures of (a) LDH-OsO_4, (b) resin-OsO_4, (c) SiO_2-OsO_4.

1. Asymmetric Dihydroxylation of Olefins Using LDH-OsO_4. In an effort to widen the scope and application of immobilized catalysts, various supports, solvents, and cooxidants were tested. The heterogeneous AD of olefins using exchanger-OsO_4 catalysts was performed in H_2O-^{t}BuOH using NMO, $K_3Fe(CN)_6$, and molecular oxygen as cooxidants. LDH-OsO_4 displays superior activity over other ion-exchangers in the dihydroxylation of *trans*-stilbene. Further, the LDH-OsO_4 efficiently dihydroxylates a wide and varied class of olefins with comparable yields and ee's as reported with homogeneous systems.[13a] The effect of various compositions of LDH-OsO_4 catalysts, solvents, and cooxidants on AD of olefins was studied to provide an in-depth knowledge of the nature of the LDH support. First, the LDH-OsO_4 catalysts were prepared by varying the ratio of M(II)/M(III) and the interlayer anion. These catalysts were subjected to AD of *trans*-stilbene (Table 1). The variation of the Mg/Al ratio from 2 to 3 resulted in a slight improvement in activity, but the replacement of Mg by Ni in the framework did not alter the activity of the catalyst. Next, we studied the effect of various interlayer co-anions unexchanged/introduced on the LDH-OsO_4 (0.12 mmol/g) in AD reactions. The OAc^-, CO_3^{2-} anions were introduced through the exchange of remnant Cl^- anions in LDH-OsO_4 by stirring it with an aqueous solution

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Table 1. Dihydroxylation of *trans*-Stilbene Using LDH-OsO_4 with Various Compositions[a]

M^1–M^{11} (M^1/M^{11})	X (interlayer co-anion)	yield (%)
Mg−Al (2)	Cl	85
Mg−Al (3)	Cl	87
Mg−Al (3)	NO_3	60
Mg−Al (3)	OAc	94
Mg−Al (3)	CO_3	96
Ni−Al (3)	Cl	87

[a] The *trans*-stilbene (1 mmol), NMO (1.3 equiv), and LDH-OsO_4 (1 mol %) in H_2O-acetone (1:3, 6 mL) were stirred at room temperature for 2 h.

Table 2. Effect of Loading on the LDH-OsO_4-Catalyzed Dihydroxylation of *trans*-Stilbene[a]

entry	mmol/g	yield (%)
1	0.97	96
2	0.70	95
3	0.48	94
4	0.38	95
5	0.12	96

[a] The *trans*-stilbene (1 mmol), NMO (1.3 equiv), and LDH-OsO_4 (1 mol %) in H_2O-acetone (1:3, 6 mL) were stirred at room temperature for 2 h.

Table 3. Solvent Effect on the LDH-OsO_4-Catalyzed AD of *trans*-Stilbene[a]

entry	solvent	yield (%)	ee (%)
1	H_2O-acetone (1:3)	96	93
2	H_2O-CH_3CN-acetone (1:1:1)	93	91
3	H_2O-CH_3CN (1:3)	58	90
4	H_2O-^{t}BuOH (1:3)	62[b]	99

[a] The *trans*-stilbene (1 mmol), NMO (1.3 equiv), $(DHQD)_2PHAL$ (1 mol %), and LDH-OsO_4 (1 mol %) in the reaction solvent (6 mL) were stirred at room temperature for 2 h. [b] 95% yield for 6 h.

of NaOAc and Na_2CO_3, respectively. The activity is found to increase proportionally with the basicity of the co-anion of the catalyst, while ee remains the same (93%). The order of activity is $CO_3^{2-} > OAc^- > Cl^- > NO_3^-$. This activity trend is attributed to the faster hydrolysis of osmium monoglycolate ester under more basic conditions.

Table 2 shows the effect of osmium loading on the activity of LDH-OsO_4 in the AD of *trans*-stilbene. Near identical activities are shown irrespective of the loading levels of osmate in the LDH-OsO_4 catalyst which are in the range of 0.12−0.97 mmol g^{-1} while maintaining 1 mol % of osmate in the reactions. The rate of the reaction is proportional to the osmium content of the catalyst. These results indicate that the reaction does not experience any diffusion problem, which is ascribed to the presence of the osmium at the edge positions. As there is no diffusion problem, we employed the LDH-OsO_4 with maximum osmium loading (0.97 mmol/g) in all the AD reactions to keep the total mass of the support minimum. Similarly, identical ee's (93%) are observed irrespective of the loading levels of osmium in the LDH-OsO_4 catalyst employed in the AD reaction of *trans*-stilbene.

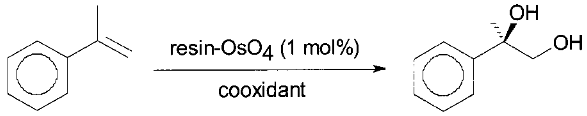
We also examined the effect of solvent on activity and enantioselectivity in the LDH-OsO_4-catalyzed dihydroxylation of *trans*-stilbene using NMO as the cooxidant (Table 3). H_2O-acetone and H_2O-CH_3CN-acetone proved to be good solvents for obtaining high yields. However, H_2O-^{t}BuOH is found to be the best solvent to obtain high enantioselectivities similar to that obtained in the case of homogeneous catalysis,[9] and the order is found to be H_2O-CH_3CN < H_2O-CH_3CN-acetone < H_2O-acetone < H_2O-^{t}BuOH.

Table 4. Dihydroxylation of α-Methylstyrene Using LDH-OsO_4[a]

cooxidant	isolated yield (%) 1st run	2nd run	3rd run
NMO	89	94	92
$K_3Fe(CN)_6$	91	54	2
O_2	93	3	

[a] The α-methylstyrene (1 mmol) and LDH-OsO_4 (1 mol %) in H_2O-^{t}BuOH were stirred with cooxidant for 6−16 h.

Scheme 3. Resin-OsO_4-Catalyzed Dihydroxylation of α-Methylstyrene



We then investigated the recyclability of LDH-OsO_4 with various cooxidants in the dihydroxylation of α-methylstyrene (Table 4). NMO is found to be a very good cooxidant for the LDH-OsO_4-catalyzed dihydroxylations. Although LDH-OsO_4 shows excellent activity for a number of cycles with NMO as the cooxidant, rapid deactivation during recycles is observed while using $K_3Fe(CN)_6$ and molecular oxygen as the cooxidants. The deactivation in the case of $K_3Fe(CN)_6$ is attributed to the displacement of OsO_4^{2-} by the competing anions that include ferricyanide and ferrocyanide. Similarly, in the case of molecular oxygen, the loss of activity observed with used catalyst is ascribed to the competitive exchange of phosphate ions during the AD reaction. These results of anion selectivities are consistent with the exchange properties of LDH, in which trivalent anions are preferred over the bivalent and monovalent anions.[19]

2. Asymmetric Dihydroxylation of Olefins Using Resin-OsO_4 and SiO_2-OsO_4. To address the serious issue of leaching of the precious and toxic OsO_4^{2-} from the support in the presence of trivalent $Fe(CN)_6^{3-}$ and PO_4^{3-}, we designed and prepared resin-OsO_4 and SiO_2-OsO_4 catalysts by the ion-exchange process on the quaternary ammonium-anchored resin and silica, respectively, for AD reaction of olefins with various cooxidants, as these ion-exchangers are expected to prefer bivalent anions over trivalent anions. A cross-linked polymer was used as a precursor for the preparation of the quaternary ammonium anionic exchange resin to enhance heterogeneity in the varied solvent systems for the easy separation of resin-OsO_4 from the dihydroxylation reaction medium. Accordingly, we used a swellable, chloromethylated styrene-divinylbenzene copolymer as a source for the preparation of resin-bound osmium catalyst, which is insoluble in a variety of reaction solvents and can be recovered from the reaction by simple filtration. We chose to examine resin-OsO_4 for the achiral dihydroxylation of α-methylstyrene using various cooxidants (Scheme 3 and Table 5). As expected, resin-OsO_4 and SiO_2-OsO_4 show consistent performance for a number of recycles irrespective of the cooxidants used in the AD reaction. The resin-OsO_4 catalyst, however, displays higher activity than the SiO_2-OsO_4 catalyst. The higher activity is correlated to the swelling properties associated with the resins that enable easy access of the ligand and substrate to the OsO_4 situated inside the pores.

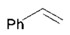
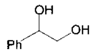
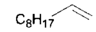
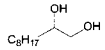
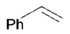
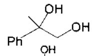
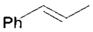
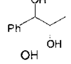
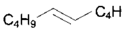
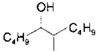
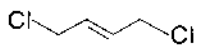
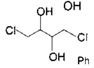
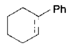
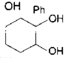
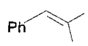
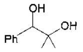
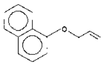
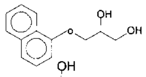
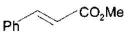
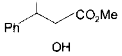
As the resin-OsO_4 is found to show slightly better activity over silica-OsO_4, we further explored the use of resin-OsO_4 initially in achiral dihydroxylation of various olefins using NMO

Table 5. Dihydroxylation of α-Methylstyrene Using Resin-OsO_4 with Various Cooxidants[a]

	yield (%)				
cooxidant	1st run	2nd run	3rd run	4th run	5th run
NMO	93	92	94	93	92
$K_3Fe(CN)_6$	92	91	93	92	90
O_2	99	97	98	99	99

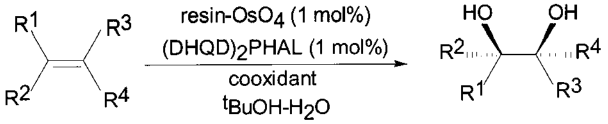
[a] The α-methylstyrene (1 mmol) and resin-OsO_4 (1 mol %) in H_2O-^{t}BuOH were stirred with cooxidant for 6−16 h.

Table 6. Dihydroxylation of Olefins Using Resin-OsO_4[a]

Entry	Olefin	Product	Isolated yield (%)
1			95
2			90
3			93
4			92
5[b]			88
6[b]			93
7[b]			90
8[b]			92
9[b]			88
10			89

[a] The olefin (1 mmol), NMO (1.3 equiv), and resin-OsO_4 (1 mol %) in H_2O-acetone (1:3, 6 mL) were stirred at room temperature for 2−8 h. [b] Two equivalents of TEAA are used.

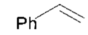
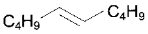
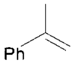
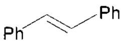
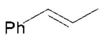
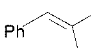
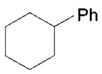
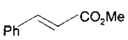
Scheme 4. Resin-OsO_4-Catalyzed AD of Olefins



cooxidant (Table 6). In a general experimental procedure, a mixture composed of olefin, NMO, and 1 mol % of the catalyst in H_2O-acetone (1:3) was stirred at room temperature. After completion of the reaction as monitored periodically by thin-layer chromatography, the catalyst was filtered and washed with ethyl acetate to obtain the corresponding diol. As can be seen from Table 6, various olefins including cyclic and acyclic, mono-, di-, and trisubstituted olefins are smoothly dihydroxylated in higher yields. Higher activity is observed with aqueous acetone as a solvent, which may be due to the better swelling of the resin observed in acetone as compared with alcoholic solvents.

Encouraged by these promising results, we then performed AD of olefins including cyclic and acyclic, mono-, di-, and trisubstituted olefins with various cooxidants, viz., NMO, $K_3Fe(CN)_6$, or oxygen using resin-OsO_4 as the catalyst in the presence of Sharpless ligands (Scheme 4), and the results are summarized in Table 7. Among the various chiral ligands available for dihydroxylation in the literature, the phthalazine class of ligands is found to be ideal for achieving higher ee's for a variety of olefins.[1] When the olefin was slowly added over a period of 12 h to a mixture of resin-OsO_4, 1,4-bis(9-*O*-dihydroquinidinyl)phthalazine ($(DHQD)_2PHAL$) (1 mol % each), and NMO, the desired diol was obtained in higher yields and enantiomeric excess (ee). Slow addition of olefin to keep the olefin concentration at a minimum level is warranted in the case of NMO to attain higher enantioselectivities thereby minimizing the second cycle, which is responsible for the lower ee's. For example, with the slow addition of α-methylstyrene, the corresponding diol is obtained with 91% ee as against the 68% ee observed when the olefin was added in one portion at the beginning of the reaction itself. These are in agreement with the earlier observations.[9] In most cases, the AD reaction mediated by resin-OsO_4/NMO offers desired diols in higher yields and enantioselectivities similar to that obtained in the homogeneous catalysis. Using the resin-OsO_4/NMO, the trisubstituted olefin, 1-phenylcyclohexene is also dihydroxylated to the corresponding diol with 91% ee in the presence of tetraethylammonium acetate (TEAA) or $CH_3SO_2NH_2$ additives (Table 7, entry 9). This phenomenon substantiates that the hydrolysis of osmate ester, a pronounced slow process in case of trisubstituted olefin, is accelerated with the use of an additive to afford higher ee. These are in conformity with the earlier observations.[9]

Table 7. Asymmetric Dihydroxylation of Olefins with Resin-OsO_4 Using Various Cooxidants[a]

Entry	Olefin	Cooxidant					
		NMO		$K_3Fe(CN)_6$		O_2	
		yield(%)	ee(%)	yield(%)	ee(%)	yield(%)	ee(%)
1		92	95	89	97	50	89
2		94	67[b]	92	95[c]	91	88
3		93	91	92	93	99	84
4[d]		90	90	88	93	97	82
5[e]		92	99	95	99	20	92
6[d,e]		89	99	91	99	17	91
7		95	96	92	98	47	86
8		95	92[b]	90	92[c]	53	87
9		90	91[b]	88	99[c]	80	90
10		94	98	92	99	-	-

[a] All reactions were carried out with 1 mol % of resin-OsO_4 and 1 mol % of $(DHQD)_2PHAL$ for 12−24 h. In case of NMO as the cooxidant, olefin was added slowly over a period of 12 h. The ee was determined by HPLC analysis. [b] Two equivalents of TEAA were used. Olefin was added slowly over a period of 20 h. [c] One equivalent of $CH_3SO_2NH_2$ was used. [d] Results obtained with SiO_2-OsO_4 catalyst. [e] Five milliliters of ^{t}BuOH in excess was employed.

The present resin-OsO_4 is superior in terms of activity, enantioselectivity, and the scope of the reaction in comparison with that of Kobayashi poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS)-MC OsO_4 and phenoxyethoxymethyl-polystyrene (PEM)-MC OsO_4 catalysts. For example, the present resin-OsO_4 catalyst is 30-fold more active than the Kobayashi catalyst (ABS-MC OsO_4) in the achiral dihydroxylation of *trans*-*β*-methylstyrene conducted under similar conditions.

The resin-OsO_4/$K_3Fe(CN)_6$/K_2CO_3 system offers excellent yields and ee's for acyclic, cyclic, mono-, di-, and trisubstituted olefins without resorting to slow addition of the olefin. Further, resin-OsO_4 also afforded excellent yields and ee's when $K_3Fe(CN)_6$ and K_2CO_3 were charged in one portion at the beginning of the reaction. On the other hand, the Kobayashi PEM-MC OsO_4 catalyst gives moderate to good yields despite the controlled addition of $K_3Fe(CN)_6$ and K_2CO_3. For example, in the case of 5-decene, *trans*-stilbene, and methyl cinnamate, the resin-OsO_4-$K_3Fe(CN)_6$ system gives 92, 95, and 92% yields as compared with 41, 66, and 51% yields, respectively, while using PEM-MC OsO_4 catalyst. The products of these substrates are important intermediates for the preparation of several chiral ligands and drugs. The present system offers distinctly higher enantioselectivities (i.e., 97 and 93% as compared with the 78 and 76% observed with PEM-MC OsO_4) for styrene and α-methylstyrene, respectively (Table 7, entries 1, 3). Unlike the Kobayashi catalyst, the heterogeneity of resin-OsO_4 irrespective of the solvents used allows us to employ H_2O-^{t}BuOH enabling easy separation and higher ee's in the AD reaction.

Finally, we employed molecular oxygen as the cooxidant, as it is inexpensive, environmentally friendly, and the most attractive candidate for the AD reaction of various olefins catalyzed by the resin-OsO_4 under atmospheric conditions. Considering the slightly basic nature of the support, we tested the dihydroxylation of α-methylstyrene in aqueous butanol with the aid of an oxygen balloon and found the yield of the diol to be dismal. When the pH of the reaction is increased to 10.4 using phosphate buffer, the yield is quantitative which is in consonance with the results observed by Beller et al. in homogeneous reactions.[11] No reaction was observed at room temperature. Hence, optimum temperature in the range of 40−50 °C is necessary to obtain good yields. Under identical conditions, the turnover number for the heterogeneous catalyst is almost similar to the homogeneous system.

Molecular oxygen served as a better cooxidant for aliphatic olefins and aromatic olefins with no α hydrogen atom. The lower chemoselectivity toward diol in the case of aromatic olefins containing α hydrogens is attributed to the overoxidation of benzylic hydroxyls formed during dihydroxylation. Similarly, the heterogeneous system developed here is ineffective for the dihydroxylation of olefins containing ester functions. The lower ee with molecular oxygen as compared to $K_3Fe(CN)_6$ and NMO is attributed to the higher reaction temperatures and higher pH required in the former system to obtain reasonable reactivity.

Resin-OsO_4 and SiO_2-OsO_4 catalysts exhibit good performance for a number of recycles irrespective of the cooxidant used. The catalysts were recovered quantitatively by simple filtration, and the chiral ligand was also recovered by simple acid/base extraction (>95% recovery). The recovered resin-OsO_4, charged along with the replenished chiral ligand to make up to 1 mol %, is reused for five cycles, and consistent activity and enantioselectivity are noticed (Figure 2). When the dihydroxylation reaction was conducted with the filtrate of the completed reaction, no activity was found. The display of robustness of resin-OsO_4 and SiO_2-OsO_4, especially in the case of $K_3Fe(CN)_6$ and molecular oxygen in achiral and asymmetric dihydroxylation, is attributed to the exactly opposite ion-exchange behavior of the quaternary ammonium form of resin and silica materials as compared to the LDH support. The fundamental difference between these two types of anion-exchange materials arises from hydration effects and is in agreement with the ion selectivities noticed earlier.[19] Because of its insoluble nature, the resin-OsO_4 catalyst can be simply filtered irrespective of the solvent used in the reaction and hence finds wider applicability than the Kobayashi catalysts.

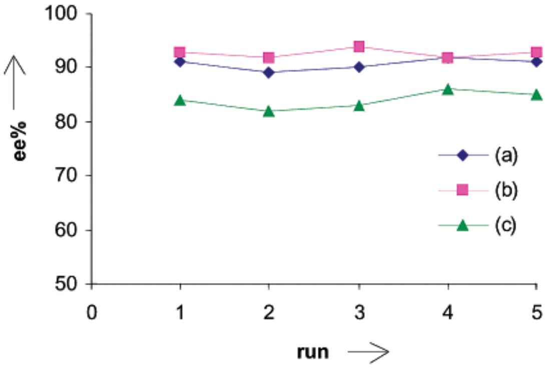


Figure 2. Enantioselectivities obtained in multiple uses of the resin-OsO_4 catalyst in the asymmetric dihydroxylation of α-methylstyrene with (a) NMO, (b) $K_3Fe(CN)_6$, and (c) O_2 as cooxidants. Recovery of osmium is quantitative, and recovery of $(DHQD)_2PHAL$ = 95%. Yields in run 1 are with fresh catalysts, and those in runs 2−5 are with reused catalysts.

We then examined the effect of L/Os (ligand:osmium) on ee's using NMO, $K_3Fe(CN)_6$, and molecular oxygen and observed that the equimolar ratio is sufficient for achieving higher ee's and an increase in the ratio of L/Os to 3 did not show any improvement in the ee of the diol. In this heterogeneous system, excellent ee's are thus achieved with an equimolar ratio of ligand to osmium in contrast to the homogeneous reaction wherein a 2−3 molar excess of expensive chiral ligand to osmium is usually employed.[1,9−12] These studies indicate that the binding ability of the present heterogeneous osmium catalyst with chiral ligand is greater than the homogeneous analogue.

We also examined the effect of solvent on activity and enantioselectivity in the dihydroxylation of styrene using resin-OsO_4 and silca-OsO_4 with NMO as a cooxidant. The similar trends in terms of activity and ee's are noticed as observed with LDH-OsO_4 and homogeneous OsO_4 systems, thus indicating that the support did not show any adverse effect in AD reactions, despite the use of varied supports with different characteristics ranging from hydrophilic (LDH) to hydrophobic (silica) to highly hydrophobic (resin).

The complexation of the large chiral ligand, $(DHQD)_2PHAL$, is a prerequisite to afford asymmetric induction. The higher enantioselectivities obtained using the supported osmium catalysts and the absence of diffusion problem as discussed above substantiate the location of osmate on the surface in all of the exchangers. The large positive electric potential of the exchanger-OsO_4 surface induces an enrichment of cooxidants close to the surface. Similarly, the olefin also builds up its concentrations close to the surface, as is evident from the experiments, to indicate that the olefin has a high adsorption coefficient on the support surface. Apart from this, spatial organization and electrical shielding[24] are responsible for the superior performance of the exchanger-OsO_4 catalysts over the homogeneous osmium catalysts. The practice of similar protocols such as administering slow addition of olefin and use of additive in the

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(24) Voet, D.; Voet, J. G. *Biochemistry*, 2nd ed.; Wiley & Sons: New York, 1995; Chapter 14.

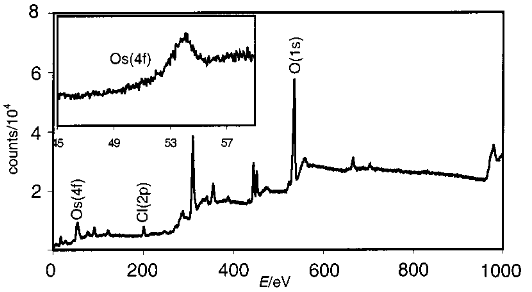
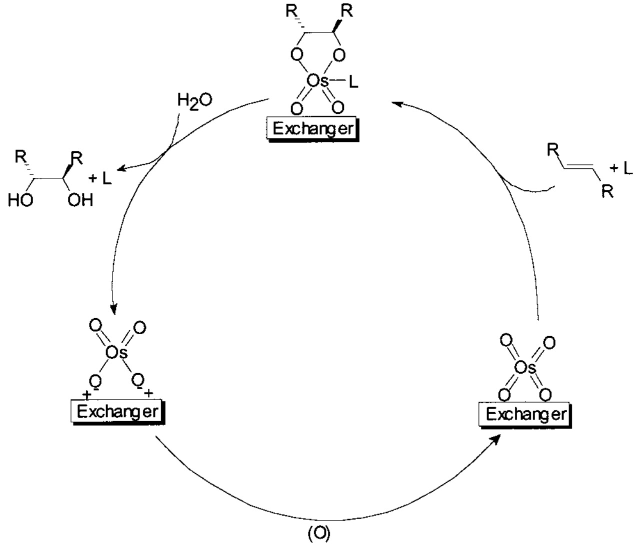


Figure 3. XPS-spectrum of LDH-OsO_4 recovered after the reaction.

Scheme 5. Plausible Mechanism for the Exchanger-OsO_4-Catalyzed Dihydroxylation of Olefins



case of trisubstituted olefin as in homogeneous reactions required to obtain higher ee indicates that the active species is the same in the exchanger-OsO_4 catalyst as in homogeneous reactions. The IR and UV-DRS spectra indicate that the OsO_4^{2-} remains unchanged during the exchange process. The exchanged osmate is also observed with X-ray photoelectron spectroscopy (XPS). The Os $4f_{7/2}$ line at 53.04 eV confirms the +VI oxidation state of osmium. On the basis of the reported value, this is clear evidence that the osmate is unchanged during ion-exchange.[25] The used catalyst also shows a $4f_{7/2}$ line at 53.04 eV (Figure 3), indicating the osmium is finally reduced after completion of the AD reaction, and thus the plausible mechanism may proceed by a path identical to that mediated by potassium osmate (Scheme 5). The oxidation of exchanger-OsO_4 with cooxidant forms the osmium (VIII) complex, which interacts with the chiral ligand and olefin to form osmium monoglycolate ester. The hydrolysis of the osmium monoglycolate ester results in the formation of diol with the regeneration of the active catalyst.

The AD experiments were conducted to find out the heterogeneity of catalyst in conjunction with the use of various cooxidants. It is observed that LDH-OsO_4 suffers from leaching of precious osmium metal when $K_3Fe(CN)_6$ or oxygen is used as a cooxidant. On the other hand, the resin-OsO_4 and SiO_2-OsO_4 are found to be very robust and heterogeneous throughout the AD reaction irrespective of the cooxidant used wherein no leaching of Os is observed either during or at the end of the reaction. It is interesting to note that the exchanger holds both the OsO_4^{2-} and the Os(VIII) species possibly through electrostatic interactions. The other possibility could be that the reduction of Os(VIII) to Os(VI) is too fast to detach neutral OsO_4 from the support. However, when exchanger-OsO_4 is treated with the oxidant in the absence of olefin, osmium is found to leach from the support which indicates that the exchanger-OsO_4 catalysts are not stable in the oxidative environment.

Conclusions

The exchanger-OsO_4 catalysts are successfully employed for the AD of olefins to afford the diols with higher yields and ee's that are similar to the homogeneous process. Various cooxidants such as *N*-methylmorpholine *N*-oxide (NMO), $K_3Fe(CN)_6$, and molecular oxygen are explored for the AD reaction in heterogeneous conditions. Among the heterogeneous osmium catalysts, the OsO_4^{2-} exchanged onto LDH displays excellent activity with NMO as the cooxidant, but the resin-OsO_4 shows good performance in terms of catalyst recovery and reusability irrespective of the cooxidant employed. The possible large-scale synthesis of diols employing the heterogeneous catalyst using NMO as the cooxidant minimizes the solid waste effluent at least in the case of the aromatic olefins. For the aliphatic olefins, the best cooxidant is $K_3Fe(CN)_6$, and optionally molecular oxygen also serves to achieve higher ee's for certain olefins. The simple procedure, easy recovery, and reusable catalytic systems are expected to contribute to the development of benign chemical processes and products.

Experimental Section

General. IR spectra for samples as KBr pellets were recorded on a BIORAD 175C FTIR spectrometer. Diffuse reflectance UV spectra for samples as KBr pellets were recorded on a GBC cintra 10e UV−vis spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. Chemical shifts (δ) are reported in ppm, using TMS and $CDCl_3$ as internal standards for ^1H NMR and ^{13}C NMR, respectively. X-ray powder diffraction (XRD) data were collected on a Siemens/D-5000 diffractometer using Cu Kα radiation ($\lambda = 1.5405$ Å). Specific surface areas are calculated from BET nitrogen isotherms determined at −196 °C (Micromeritics ASAP 2000) on samples degassed at 250 °C for 12 h before the experiment. SEM-EDX (scanning electron microscopy-energy-dispersive X-ray analysis) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. High performance liquid chromatography (HPLC) was performed using the following apparatus: SHIMADZU LC-10AT (liquid chromatograph), SHIMADZU SPD-10A (UV detector), and SHIMADZU C-R6A Chromatopac. ACME silica gel (100−200 mesh) was used for column chromatography, and thin-layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates. Optical rotations were obtained on a Jasco P-1020 Polarimeter and reported as follows $[\alpha]^{\text{temperature}}_{\text{wavelength}}$, concentration ($c$ = g/100 mL), and solvent. Slow additions of olefins were carried out using a syringe pump.

$K_2OsO_4 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, TEAA, $(DHQD)_2PHAL$, and NMO were purchased from Aldrich. Allyl 1-naphthyl ether and ethyl (4-methoxyphenyl) cinnamate were prepared, while the other olefins were purchased from Aldrich. All the other solvents and chemicals were obtained from commercial sources and used as such without further purification.

Preparation of Catalysts. The preparation of LDH (Mg−Al−Cl) was based on literature procedure.[17b] A mixture of $MgCl_2 \cdot 6H_2O$ (30.49 g, 0.15 mmol) and $AlCl_3 \cdot 6H_2O$ (12.07 g, 0.05 mmol) was dissolved in

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(25) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomden, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Minnesota, 1992.

200 mL of deionized water. To this aqueous solution was slowly added 100 mL of NaOH (2 M) solution at 25 °C, and a further amount of 2 M NaOH solution was added to maintain a pH of 10 under nitrogen flow. The resulting suspension was stirred overnight at 70 °C. The solid product was isolated by filtration, washed thoroughly with deionized water, and dried overnight at 80 °C. All of the synthetic steps were carried out using decarbonated water.

LDH-OsO$_4$. One and one-half grams of Mg−Al−Cl was suspended in 150 mL of 0.689 g (1.87 mmol) aqueous potassium osmate solution and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water, and vacuum-dried to obtain 1.916 g of LDH-OsO$_4$ (0.975 mmol of Os per g).

Resin-OsO$_4$. Resin was obtained by quaternization of triethylamine (2.1 mL, 21 mmol) with 1 g of chloromethylated styrene-divinylbenzene copolymer (Merrifield resin, capacity ∼2.1 mequiv/g) in chloroform (20 mL) under reflux for 24 h. One gram of quaternary ammonium resin was suspended in 100 mL of 0.8 mmol aqueous potassium osmate solution and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 300 mL of water, and vacuum-dried to obtain resin-OsO$_4$ (0.641 mmol of Os per g).

SiO$_2$-OsO$_4$. Modified silica was obtained by quaternization of triethylamine (0.7 mL, 7 mmol) with bromopropylsilica (capacity 0.7 mequiv/g) in chloroform (20 mL) under reflux for 24 h. One gram of quaternary ammonium silica was suspended in 100 mL of 0.33 mmol aqueous potassium osmate solution and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 300 mL of water, and vacuum-dried to obtain SiO$_2$-OsO$_4$ (0.317 mmol of Os per g).

General Procedure for Dihydroxylation of Olefins. An olefin (1 mmol), exchanger-OsO$_4$ (0.01 mmol), and *N*-methylmorpholine *N*-oxide (NMO, 1.3 mmol) were taken in a round-bottomed flask containing H$_2$O-acetone (1:3, 6 mL) and stirred for 2−8 h at room temperature. After completion of the reaction (checked by TLC), the exchanger-OsO$_4$ catalyst was filtered and washed with ethyl acetate. After removing the solvent, the crude material was chromatographed on silica gel to afford the corresponding cis-diol.

Asymmetric Dihydroxylation of Olefins Using Exchanger-OsO$_4$. Using NMO as the Cooxidant. Resin-OsO$_4$ (15.6 mg, 0.01 mmol), (DHQD)$_2$PHAL (7.8 mg, 0.01 mmol), and *N*-methylmorpholine *N*-oxide (NMO, 1.3 mmol) were taken in a round-bottomed flask containing ^{t}BuOH-H$_2$O (3:1, 6 mL) and stirred at room temperature. To this mixture was slowly added an olefin (1 mmol) for 12 h. After completion of the reaction, the resin-OsO$_4$ catalyst was filtered and washed with ethyl acetate. The combined organics were washed with 1 N HCl to recover the chiral ligand from the aqueous layer. After removing the solvent, the crude material was chromatographed on silica gel to afford the corresponding cis-diol.

Using K$_3$Fe(CN)$_6$ as the Cooxidant. Resin-OsO$_4$ (15.6 mg, 0.01 mmol), (DHQD)$_2$PHAL (7.8 mg, 0.01 mmol), K$_3$Fe(CN)$_6$ (3 mmol), K$_2$CO$_3$ (3 mmol), and olefin (1 mmol) were taken in a round-bottomed flask containing ^{t}BuOH-H$_2$O (1:1, 10 mL) and stirred at room temperature for 12−24 h. After completion of the reaction, the catalyst was filtered and washed with ethyl acetate. After removing the solvent, the crude material was chromatographed on silica gel to afford the corresponding cis-diol.

Using Molecular Oxygen as the Cooxidant. Resin-OsO$_4$ (15.6 mg, 0.01 mmol) and (DHQD)$_2$PHAL (7.8 mg, 0.01 mmol) in a round-bottomed flask containing aqueous buffer solution (12.5 mL, pH 10.4) and ^{t}BuOH (5 mL) were stirred at 1 bar O$_2$ and 50 °C in an oil bath. An olefin (1 mmol) was then added in one portion, and the reaction mixture was stirred vigorously with a magnetic stirring bar. After completion of the reaction (16−24 h as monitored by TLC), the catalyst was filtered and washed with ethyl acetate. After removing the solvent, the crude material was chromatographed on silica gel to afford the corresponding cis-diol.

Reuse of Catalysts. The reusability of resin-OsO$_4$ catalyst was carried out by performing the AD of α-methylstyrene on a 10 mmol scale. After completion of the reaction, the catalyst was recovered by filtration and subsequently washed with ethyl acetate. The recovered catalyst was reused for five runs. Recovery of osmium is quantitative, while recovery of (DHQD)$_2$PHAL is 95%.

Heterogeneity Tests. Experiment 1. A mixture of LDH-OsO$_4$ (0.01 mmol) and *N*-methylmorpholine *N*-oxide (NMO, 1.3 mmol) in ^{t}BuOH-H$_2$O (3:1, 6 mL) was stirred for 24 h at room temperature and filtered. To the filtrate was added α-methylstyrene, and the mixture was stirred for 3 h. The diol was obtained in 70% yield. Similarly, the reactions conducted with filtrates obtained by pretreatment of LDH-OsO$_4$ with NMO for 5 min and 1 h gave the diols with 0.2% and 50% yield in 3 h. The results clearly show that the catalyst suffers from leaching of osmium upon treatment with cooxidant.

Experiment 2. A mixture of the LDH-OsO$_4$, α-methylstyrene, and NMO in ^{t}BuOH-H$_2$O was stirred for 3 h. After completion of the reaction, the catalyst was separated by filtration. To one part of the filtrate were added fresh α-methylstyrene and NMO, and the mixture was stirred for 24 h. There was no reaction with the fresh α-methylstyrene. To the second part of the solution were added a different olefin, *trans*-stilbene, and NMO, and the mixture was stirred for 24 h. No stilbene diol was formed. These results strongly suggest that the OsO$_4$ is bound to the support during the reaction when all the constituents are present.

It appears that during oxidation with NMO, the anionic form of OsO$_4$ transforms into a Os(VIII) species, but is bound on LDH through electrostatic interaction. The LDH-supported Os(VIII) species reacts with olefin to form osmium(VI) monoglycolate ester and subsequently to give the OsO$_4^{2-}$ anion bound to LDH with the liberation of the product. It is proved that OsO$_4^{2-}$ is bound to the LDH during the reaction, and the stability of the catalyst is established. These observations are in agreement with the LDH-WO$_4$-catalyzed oxidative bromination reaction.[14b]

Experiment 3. (a) LDH-OsO$_4$ was stirred with NMO for 24 h in ^{t}BuOH-H$_2$O. *trans*-Stilbene was then added, and this mixture was stirred for 6 h. After completion of the reaction, the catalyst was removed by filtration. Two separate experiments were conducted both with recovered catalyst and with filtrate as described. A mixture of the recovered catalyst, α-methylstyrene, and NMO in ^{t}BuOH-H$_2$O was stirred for 3 h. The diol was obtained in 10% yield. To the filtrate were added α-methylstyrene and NMO, and the mixture was stirred at room temperature for 3 h. The diol was obtained in 80% yield. (b) Resin-OsO$_4$ was stirred with K$_3$Fe(CN)$_6$ (3 mmol), K$_2$CO$_3$ (3 mmol), and ^{t}BuOH-H$_2$O (1:1, 10 mL) at room temperature for 24 h. α-Methylstyrene was then added, and this mixture was stirred for 12 h. After completion of the reaction, the catalyst was removed by filtration. Two separate experiments were conducted both with the recovered catalyst and with filtrate as described. A mixture of the recovered catalyst, *trans*-stilbene, and oxidant in ^{t}BuOH-H$_2$O was stirred for 12 h. The diol was obtained in 16% yield. To the filtrate were added *trans*-stilbene and oxidant, and it was stirred at room temperature for 12 h. The diol was obtained in 72% yield.

These results strongly suggest that the leached Os species on treatment with oxidant in the absence of olefin could not be reexchanged on the support during the reaction after the addition of olefin. Similar observations were noticed with the SiO$_2$-OsO$_4$ in the identical parallel experiments (1−3) conducted in the effort to understand the heterogeneity of the catalyst.

With K$_3$Fe(CN)$_6$ as Cooxidant. Experiment 4. The reaction was conducted by stirring α-methylstyrene (1 mmol), K$_3$Fe(CN)$_6$ (3 mmol), K$_2$CO$_3$ (3 mmol), and 1 mol % of resin-OsO$_4$ in ^{t}BuOH-H$_2$O (1:1, 10 mL) at room temperature for 12 h. After completion of the reaction, the catalyst was removed by filtration, and the solution was subjected for the next reaction. To the filtrate of the completed reaction were added *trans*-stilbene (1 mmol), K$_2$CO$_3$ (3 mmol), and K$_3$Fe(CN)$_6$ (3 mmol) in ^{t}BuOH-H_2O (1:1, 10 mL), and the mixture was stirred at room temperature for 24 h. No stilbene diol was formed.

With Molecular Oxygen as the Cooxidant. Experiment 5. Resin-OsO_4 (10.2 mg, 0.01 mmol) and α-methylstyrene (1 mmol) in a round-bottomed flask containing aqueous buffer solution (12.5 mL, pH 10.4) and ^{t}BuOH (5 mL) were stirred at 1 bar O_2 and 50 °C for 16 h in an oil bath. After completion of the reaction, the catalyst was filtered, and to the filtrate were added phenylcyclohexene (1 mmol) in aqueous buffer solution (12.5 mL, pH 10.4) and ^{t}BuOH (5 mL), and the mixture was stirred at 1 bar O_2 and 50 °C for 24 h in an oil bath. No phenylcyclohexene diol was formed.

Characterization of Products. The following compounds are known compounds, and their spectra are in accordance with those reported in the literature. The enantiomeric excess of the diols was determined by HPLC analysis with chiral stationary phases.

1-Phenyl-1,2-ethanediol. ^{1}H NMR: δ 2.04 (brs, 1H), 2.46 (brs, 1H), 3.63 (dd, 1H, $J = 8.2$, 11.4 Hz), 3.72 (dd, 1H, $J = 3.6$, 11.4 Hz), 4.79 (dd, 1H, $J = 3.6$, 8.2 Hz), 7.28−7.34 (m, 5H). ^{13}C NMR: δ 68.0, 74.7, 126.0, 128.0, 128.5, 140.4. HPLC (Daicel Chiralcel OD-H, 5% $_i$PrOH in hexane, flow rate 0.5 mL/min): $t_R = 34.7$ (major), $t_R = 38.9$ (minor).

5,6-Decanediol. ^{1}H NMR: δ 0.90 (t, 6H, $J = 7.2$ Hz), 1.23−1.50 (m, 12H), 1.96 (s, 2H), 3.38 (m, 2H). ^{13}C NMR: δ 14.0, 22.7, 27.8, 33.3, 74.5. HPLC (bisbenzoate) (Daicel Chiralcel OD-H, 0.2% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 6.0$ (minor), $t_R = 7.3$ (major).

2-Phenyl-1,2-propanediol. ^{1}H NMR: δ 1.50 (s, 3H), 3.15 (brs, 2H), 3.60 (d, 1H, $J = 11.2$ Hz), 3.75 (d, 1H, $J = 11.2$ Hz), 7.24−7.44 (m, 5H). ^{13}C NMR: δ 26.0, 70.9, 74.8, 125.0, 127.1, 128.4, 145.0. HPLC (Daicel Chiralcel OJ, 10% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 9.2$ (minor), $t_R = 12.5$ (major).

1,2-Diphenyl-1,2-ethanediol. ^{1}H NMR: δ 2.73 (brs, 2H), 4.69 (s, 2H), 7.09−7.22 (m, 10H). ^{13}C NMR: δ 79.1, 126.9, 127.9, 128.1, 139.8. HPLC (Daicel Chiralcel OJ, 10% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 12.1$ (minor), $t_R = 13.3$ (major).

1-Phenyl-1,2-propanediol. ^{1}H NMR: δ 0.97 (d, 3H, $J = 6.3$ Hz), 2.65 (brs, 2H), 3.79 (dq, 1H, $J = 6.3$, 7.6 Hz), 4.28 (dd, 1H, $J = 7.6$ Hz), 7.25−7.34 (m, 5H). ^{13}C NMR: δ 18.6, 72.1, 79.4, 126.8, 127.9, 128.3, 141.0. HPLC (Daicel Chiralcel OD, 5% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 15.0$ (major), $t_R = 16.28$ (minor).

2-Methyl-1-phenyl-1,2-propanediol. ^{1}H NMR: δ 1.03 (s, 3H), 1.15 (s, 3H), 2.78 (brs, 2H), 4.43 (d, 1H), 7.23−7.35 (m, 5H). ^{13}C NMR: δ 23.4, 26.4, 73.4, 80.7, 127.4, 127.6, 127.8, 140.6. HPLC (Daicel Chiralcel OD, 2.5% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 22.8$ (major), $t_R = 27.1$(minor).

1-Phenyl-1,2-cyclohexanediol. ^{1}H NMR: δ 1.35−1.89 (m, 9H), 2.51 (s, 1H), 3.96 (dd, 1H, $J = 4.7$, 11.1 Hz), 7.21−7.53 (m, 5H). ^{13}C NMR: δ 21.1, 24.3, 30.9, 38.5, 74.5, 75.7, 125.1, 127.0, 128.5, 146.3. HPLC (Daicel Chiralcel OJ, 5% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 17.6$ (minor), $t_R = 21.9$ (major).

Methyl 2,3-Dihydroxy-3-phenylpropionate. ^{1}H NMR: δ 3.32 (br, 2H), 3.81 (s, 3H), 4.36 (d, $J = 2.8$ Hz, 1H), 5.01 (d, $J = 2.8$ Hz, 1H), 7.36 (m, 5H). ^{13}C NMR: δ 52.8, 74.4, 74.7, 126.2, 128.1, 128.4, 139.9, 173.1. HPLC (Daicel Chiralcel OJ, 10% ^{i}PrOH in hexane, flow rate 1.0 mL/min): $t_R = 19.1$ (minor), $t_R = 26.7$ (major).

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