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Immobilization of Osmium Catalysts for Asymmetric Dihydroxylation of Olefins

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Abstract: Osmium-catalyzed asymmetric dihydroxylation provides powerful synthetic routes to optically active vicinal diols from olefins with high enantioselectivity. High catalytic efficiency using only 0.2–1.0 mol% of the osmium catalyst has been attained, and the chiral ligand may be recoverable in large-scale synthesis by extraction with dilute sulfuric acid. However, in spite of the significant advances in this transformation, high toxicity and volatility of the osmium components as well as possible contamination of toxic osmium species in the products have been obstacles for industrial applications. To address this issue, considerable efforts have been devoted to immobilization of the osmium catalyst. This review summarizes several promising methods for immobilization of the osmium components, especially focusing on solid phase-supported osmium catalysts for asymmetric dihydroxylation.

Keywords: dihydroxylation; immobilization; olefins; osmium catalyst

1 Introduction

Osmium-catalyzed asymmetric dihydroxylation is undoubtedly a powerful synthetic reaction which can construct chiral vicinal diols from C=C double bonds with high enantioselectivity.[1] High catalytic efficiency has been attained; many reactions can be conducted with 0.2–1.0 mol% of the osmium catalyst, and the chiral ligand may be recoverable in large-scale synthesis by extraction with dilute sulfuric acid. Sharpless indicated in his review[1a] that three key discoveries for the rate enhancement are: (1) two-phase conditions with $K_3Fe(CN)_6$ as the stoichiometric cooxidant, (2) large acceleration by $MeSO_2NH_2$ additive for the reaction of internal alkenes, and (3) highly effective chiral ligands with two *Cinchona* alkaloid units attached to a heterocyclic spacer.

In spite of these significant advances, high toxicity and volatility of the osmium components as well as possible contamination of toxic osmium species in the products have been obstacles for industrial applications. In order to address this issue, many efforts have been devoted to immobilization of the osmium catalyst. However, use of supported chiral ligands resulted in severe leaching of osmium due to reversible coordination of the ligands to the osmium.[2] On the other hand, several promising methods for immobilization of the osmium component have recently been reported. This review summarizes those achievements especially focusing on solid phase-supported osmium catalysts for asymmetric dihydroxylation. Abbreviations for chiral ligands appear in this review are shown in Figure 1.

The catalytic cycle of asymmetric dihydroxylation with $K_3Fe(CN)_6$ cooxidant proposed by Sharpless et al. is depicted in Scheme 1.[1] Due to the high ligand acceleration system, the osmium(VIII) tetroxide (**1**)/chiral ligand (L*) complex selectively reacts with an alkene to afford osmium(VI) ester **2**. Osmate **2** is hydrolyzed under the basic conditions to release the diol product and osmium(VI) dianion **3**. Osmate **3** is then reoxidized by $K_3Fe(CN)_6$ in the aqueous media to regenerate osmium(VIII) species **4** and then **1**. One may readily expect difficulty of immobilization of the catalyst, since the catalytic cycle involves a variety of osmium species; some are non-ionic and soluble in the organic phase while the others are ionic and soluble in the aqueous phase. Especially, osmium(VIII) tetroxide (**1**) is non-ionic, volatile, and soluble in the organic phases, but can be ionic when hydrox-

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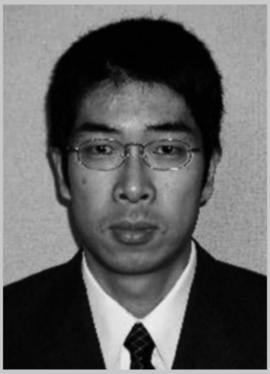


Masaharu Sugiura was born in 1970 in Tokyo and received his Ph.D. at the Tokyo Institute of Technology in 1997 under the supervision of Professor Takeshi Nakai. After postdoctoral work at Sagami Chemical Research Center (Dr. Shiro Terashima) and at the Florida State University (Professor Marie E. Krafft), he joined the research group of Professor Kobayashi as a JST postdoctoral fellow in 2000. He was appointed assistant professor in 2004, and lecturer in 2005 at the Graduate School of Pharmaceutical Sciences of the University of Tokyo. His research interests include the development of new synthetic methods and novel catalysts. He received the PSJ Award for Young Scientists in 2006.

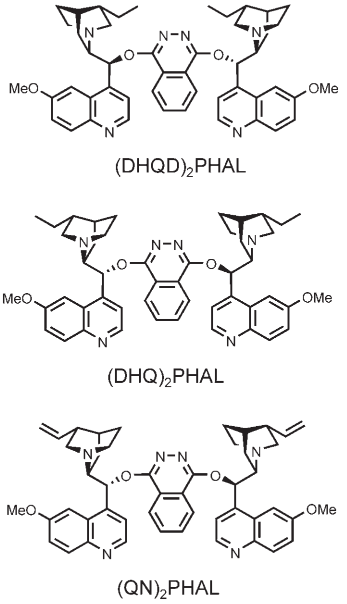
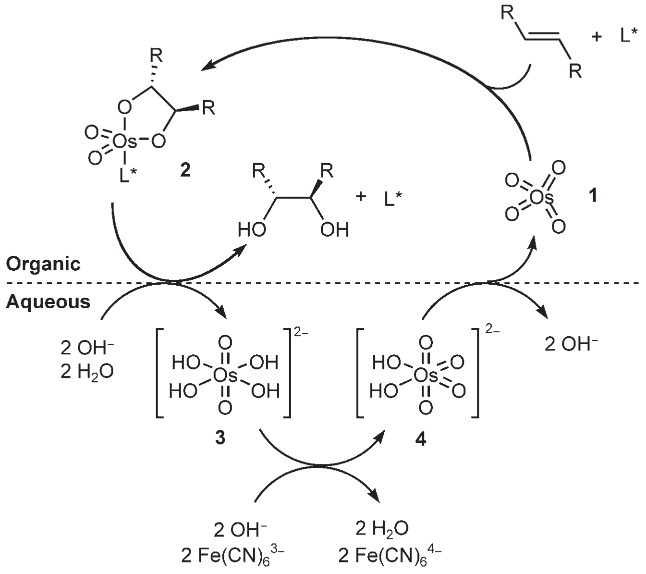


Figure 1. Abbreviations for chiral ligands.

ide ion or the chiral ligand coordinates. Another problem is involvement of the second catalytic cycle. When osmate **2** loses the chiral ligand (L*) instead of releasing the diol, the formed osmium(VI) could be reoxidized to osmium(VIII) which may oxidize the alkene substrate with low enantioselectivity. Therefore, the hydrolysis of **2** is required to be sufficiently fast, and this is dependent on the choice of the reaction system such as cooxidants and reaction media. Standing on this mechanistic ground, we survey recent developments on immobilization of the osmium catalyst.



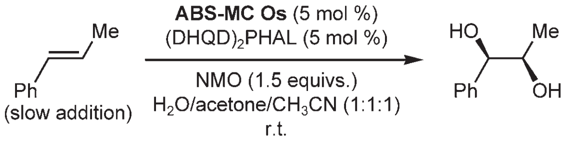
Scheme 1. The proposed catalytic cycle.

2 Microencapsulation

In 1998, we reported the microencapsulation of osmium tetroxide.[3] Microcapsules have been used for coating and isolating substances until their activity is needed, and their applications in medicine and pharmacy have been extensively studied.[4] This microencapsulation technique was applied as a method for immobilization of catalysts onto polymers. That is, catalysts would be physically enveloped by thin films of polymers, and at the same time immobilized by interaction between π electrons of the benzene rings of the polystyrene, which is used as a polymer backbone, and vacant orbitals of the catalysts (metal compounds). Following the successful example of microencapsulated scandium triflate,[5] this method was applied to prepare microcapsules including the osmium component by addition of methanol to a solution of linear polystyrene (MW = *ca.* 280,000) and osmium tetroxide in cyclohexane. This polystyrene-microencapsulated (PS-MC) Os catalyst was found to promote the non-enantioselective dihydroxylation of various simple alkenes with *N*-methylmorpholine *N*-oxide (NMO) as the cooxidant in H_2O/acetone/CH_3CN (1:1:1). The catalyst can be recovered and reused at least five times.

Since initial attempts to utilize PS-MC Os for asymmetric dihydroxylation were unsatisfactory, several polymer supports and preparative conditions were investigated. After several trials, the use of acryronitrile-butadiene-polystyrene (ABS) polymer was found to be effective.[6] ABS-MC Os was prepared by addition of methanol to a solution of ABS polymer (Stylac 200, Asashi Chemical) and osmium tetroxide in THF. The catalyst showed a good catalytic performance with NMO as a cooxidant. Recyclability was demonstrated in the reaction of β-methylstyrene; the catalyst was used five times without loss of activity and selectivity (Table 1).

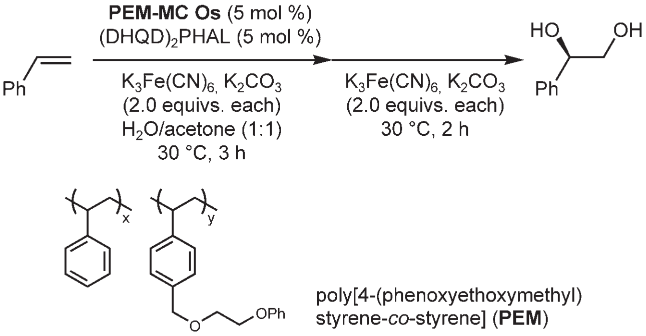
Table 1. Recycling of ABS-MC Os.



Run	Yield [%]	*ee* [%]
1	88	84
2	75	95
3	97	94
4	81	96
5	88	95

We next intended to use $K_3Fe(CN)_6$ as a cooxidant, since NMO requires slow addition of the substrate to prevent the second catalytic cycle leading to low enantioselectivity.[7] Under the conditions with $K_3Fe(CN)_6$ in *t*-BuOH/H_2O (1:1), ABS-MC Os showed good catalytic activity and was reused three times without loss of yield and selectivity. However, significant diminishment of the mass of the recovered catalyst was observed. On the other hand, polystyrene (PS) or poly(acrylonitrile-*co*-styrene) (AS) supported-MC Os showed almost no catalytic activity under these conditions. Swollen-resin magic angle spinning (SR-MAS) ^1H NMR analysis[8] of ABS-MC Os indicated that the olefin moiety derived from butadiene in the ABS polymer was oxidized by osmium to form diol units. It was speculated that the diol moiety serves as a hydrophilic part to realize effective contact of osmium species with the cooxidant under the two-phase conditions. Therefore, we explored a more effective design of the hydrophilic moiety and found that poly[4-(phenoxyethoxymethyl)styrene-*co*-styrene] (PEM) was effective as the polymer support. Although controlled addition of the cooxidant and the base was required to obtain reasonable yields, PEM-MC Os could be reused for three times with quantitative recovery (Table 2). The procedure is simple; the reaction is quenched by neutralization with 2 N H_2SO_4 followed by addition of ethanol. The catalyst is recovered by simple filtration, and reused. No leaching of the osmium in the filtrate was detected by fluorescence X-ray analysis.

Table 2. PEM-MC Os.



Run[a]	Yield [%]	*ee* [%]
1	85	78
2	66	78
3	84	78

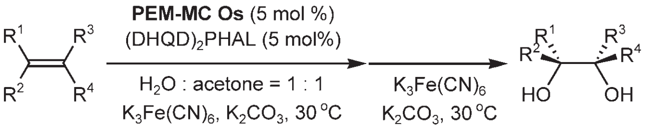
[a] The recovery of the catalyst was quantitative in all cases.

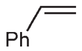
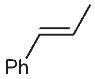
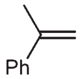
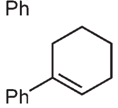
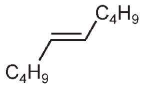
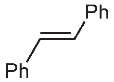
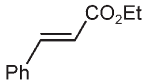
The PEM-MC Os system was applied to other olefins, and the results are summarized in Table 3. In most cases, the desired diols were obtained in good yields with high enantiomeric excesses. It is noteworthy that a wide variety of olefins are applicable in this system and that the catalyst was recovered quantitatively by simple filtration.

The asymmetric dihydroxylation using PEM-MC Os was also found to proceed in water as the sole solvent when Triton X-405, a non-ionic surfactant, was used (Table 4).[9] No controlled addition of the cooxidant and the base was required in this case.

It was further revealed that cross-linked polystyrene (PSresin, cross-linked by 1 mol% 1,4-divinylben-

Table 3. Asymmetric dihydroxylation of olefins using PEM-MC Os.



Entry	Olefin	Time [h][a]	Yield [%]	*ee* [%]
1		3+2	85 (80)[b]	78 (−82)[b]
2		3+2	86	94
3		3+2	85	76
4		5+4	85	95
5		3+2	41	91
6[c]		3+2+2+2[d]	66	>99
7[c]		3+2	51	>99

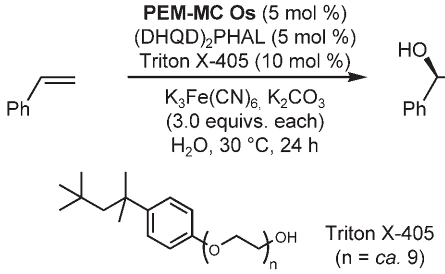
[a] $K_3Fe(CN)_6$ and K_2CO_3 were added twice. The mixture was stirred for the indicated time at each stage.

[b] $(DHQ)_2PHAL$ (5 mol%) was used instead of $(DHQD)_2PHAL$.

[c] Methanesulfonamide (1.0 equiv.) was added.

[d] One equivalent each of $K_3Fe(CN)_6$ and K_2CO_3 was added four times.

Table 4. PEM-MC Os in water.[a]

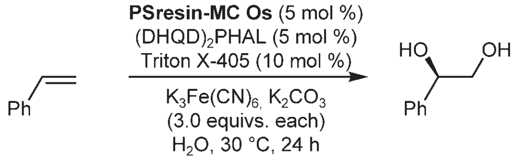


Run	Yield [%]	*ee* [%]
1	86	74
2	82	76
3	83	75

[a] In all cases, the reaction was quenched by neutralization with 2 N H_2SO_4 followed by addition of ethanol, and no leaching of osmium in the filtrate was detected by fluorescence X-ray analysis.

zene) could be used as the polymer support.[10] PSresin-MC Os showed a similar activity to PEM-MC Os and worked in water in the presence of Triton X-405 with successful recovery and reuse for five times (Table 5).

Table 5. PSresin-MC Os in water.[a]



Run	Yield [%]	*ee* [%]
1	81	78
2	84	76
3	78	77
4	86	74
5	85	72

[a] In all cases, the reaction was quenched by neutralization with 2 N H_2SO_4 followed by addition of ethanol, and no leaching of osmium in the filtrate was detected by fluorescence X-ray analysis.

The microencapsulation technique was also employed by Ley and co-workers. Osmium tetroxide was encapsulated using polyurea microcapsules by *in situ* interfacial polymerization of oil-in-water emulsions.[11] The osmium catalyst (Os EnCat) was successfully applied to the non-enantioselective dihydroxylation, but asymmetric dihydroxylation was not described.

3 Immobilization by Ionic Interaction

In 2001, Choudary and co-workers reported an ion-exchange technique for immobilization of an osmium catalyst. They employed layered double hydroxides (LDH) with the composition $Mg_{1-x}Al_x(OH)_2(Cl)_x{\cdot}zH_2O$ and quaternary ammonium salts bound to a polymer resin or a silica gel as the solid support.[12] K_2OsO_4 as an aqueous solution was introduced to these ionic supports by an ion-exchange technique to generate LDH-Os, Resin-Os, and SiO_2-Os, respectively (Figure 2).

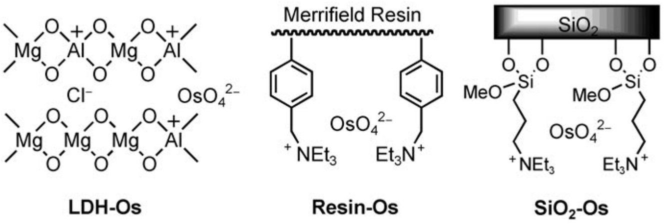
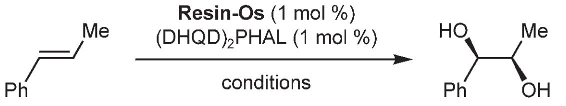


Figure 2. Ion-exchanged Os catalysts.

These immobilized catalysts were successfully applied to asymmetric dihydroxylation using NMO, $K_3Fe(CN)_6$, and even O_2 cooxidants. LDH-Os could be reused several times with NMO cooxidant, but rapid deactivation during recycle stages was observed when $K_3Fe(CN)_6/K_2CO_3$ and O_2/phosphate cooxidants were used, probably due to ion-exchange by coexisting anions. On the other hand, Resin-Os and SiO_2-Os showed superior reusability with all cooxidant systems (Table 6). The difference between these anion-exchanged materials probably arises from the hydrophobic nature of the supports: LDH (hydrophilic), SiO_2 (hydrophilic), and resin (highly hydrophobic). Resin-Os was reused five times with consistent activity and enantioselectivity.

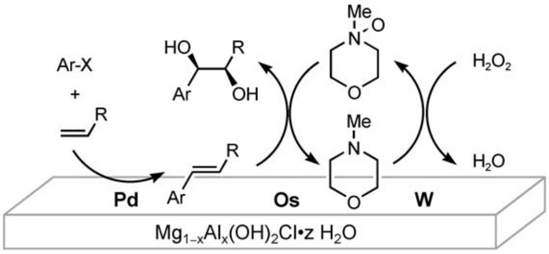
Table 6. Catalysis by Resin-Os.



Entry	Conditions	Yield [%]	*ee* [%]
1	NMO (1.3 equivs.), *t*BuOH/H_2O (3:1), r.t., 12 h (slow addition of the substrate over a period of 12 h)	95	96
		92	98
3	O_2 (1 bar), *t*BuOH, phosphate buffer (pH 10.4), 50 °C, 16–24 h	47	86

The IR and UV-DRS spectra of the ion-exchanged osmium catalysts indicate that the OsO_4^{2-} remains unchanged during the exchange process. X-ray photoelectron spectroscopy (XPS) analysis also confirmed the +VI oxidation state of osmium. The used catalyst was also shown to be Os(VI), implying that the osmium is finally reduced after completion of the reaction. When an ion-exchanged osmium catalyst was treated with the oxidant in the absence of any olefins, osmium was found to leach from the support. This indicates that the ion-exchanged Os catalysts are not stable in the oxidative environment and that the reduction of Os(VIII) to Os(VI) may be too fast to detach neutral OsO_4 from the support.

The same group applied the ion-exchange technique to attain a trifunctional catalyst for a Heck reaction/asymmetric dihydroxylation/*N*-oxidation sequence (Scheme 2).[13] Pd, Os, and W catalysts were immobilized on an LDH at the same time to give an LDH-PdOsW catalyst. The reaction sequence was carried out in one pot. A mixture of iodobenzene, styrene, triethylamine, and LDH-PdOsW (1 mol%) was stirred at 70 °C for 8 h without a solvent and a mixture of $(DHQD)_2PHAL$ (1 mol%) and *N*-methylmorpholine in *t*-BuOH/H_2O was added. Subsequently, H_2O_2 was added slowly over 12 h to afford the desired diol in 85% with 99% *ee*. The catalyst could be recovered and reused for five times with constant activity. They also reported the use of nanocrystalline magnesium oxide (MgO) as a solid support to immobilize the osmium catalyst by ionic interactions. The MgO-Os was used for the non-enantioselective dihydroxylation of olefins.[14]

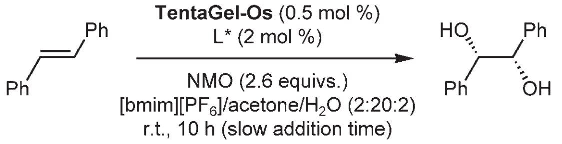


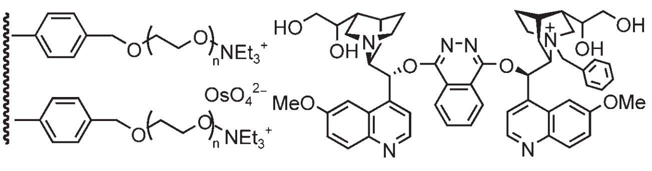
Scheme 2. A trifunctional catalyst.

The concept for immobilization of osmium catalysts by ionic interaction has been further extended to the utilization of room temperature ionic liquids as a stationary phase.[15] In these methods, recovery and reuse of the catalyst was realized by liquid-liquid phase separation. Use of supercritical CO_2 for extraction of the products was also reported.[15h,i] Hydroxylated or mono-quaternized bis-alkaloid ligands have been devised to immobilize both the osmium component and the chiral ligand in the ionic liquid phase.[15d,f,g] A room temperature ionic liquid was also utilized to immobilize a catalytic system consisting of OsO_4 and co-catalysts [*N*-methylmorpholine and a flavin, $VO(acac)_2$, or $MeReO_3$] for dihydroxylation of alkenes using H_2O_2.[15j,k] Those catalytic systems can be recycled and used up to five times.

A combined use of an osmium catalyst immobilized on quaternary ammonium salts bound to a silica gel (TentaGel-Os), mono-quaternized bis-alkaloid ligand (L*), and an ionic liquid was reported (Table 7).[16]

Table 7. TentaGel-Os/L*/ionic liquid system.





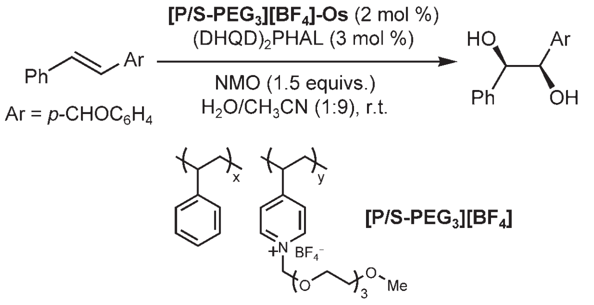
TentaGel-Os **L***

Run	1	2	3	4	5	6	7	8	9	10
Yield [%]	84	82	85	79	80	81	78	74	69	70
ee [%]	95	93	90	91	90	88	89	87	88	89

With only 0.5 mol% of the osmium catalyst and 2.0 mol% of the chiral ligand, ten recycles were achieved without significant loss of activity.

A polymer support bearing pyridinium ion moieties ([P/S-PEG$_3$][BF$_4$]) was utilized for the immobilization of osmium (Table 8).[17] The polymer was prepared from poly(4-vinylpyridine-*co*-styrene) and a triethylene glycol derivative. Osmium was introduced by shaking OsO_4 and the ionic polymer in H_2O/CH_3CN to give [P/S-PEG$_3$][BF$_4$]-Os. This catalyst exhibited good catalytic performance for asymmetric dihydroxylation and was reused five times, although a gradual loss of activity was observed.

Table 8. [P/S-PEG$_3$][BF$_4$]-Os.

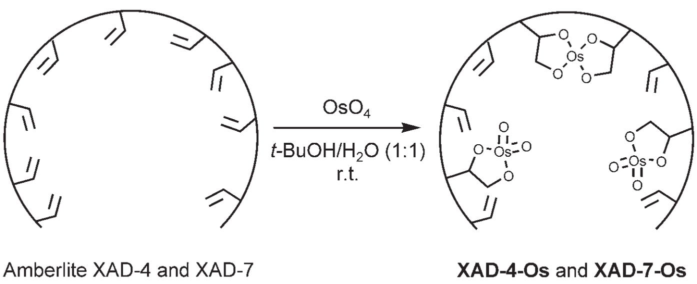


Run	Time [h]	Conversion [%]	*ee* [%]
1	3	99	96
2	4	99	96
3	6	99	97
4	10	99	97
5	12	99	96

4 Immobilization on Supports Bearing Olefins

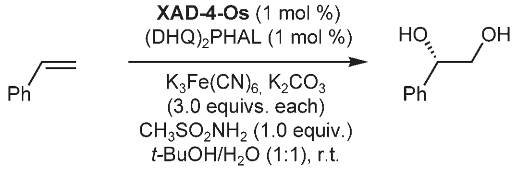
In 2001, Jacobs and co-workers reported the use of tetrasubstituted olefins on a silica gel support to immobilize osmium.[18] OsO_4 readily osmylates the tetrasubstituted olefins, but the resulting osmate(VI) ester is scarcely hydrolyzed. Therefore, the osmate(VI) is reoxidized without releasing the diol to osmate(VIII) which can serve as a catalyst *via* the second catalytic cycle. This technique was later adopted to develop soluble dendrimer-bound[19] and fluorinated[20] osmium catalysts which could be recovered and reused by phase separation. However, these methods cannot be applied to asymmetric dihydroxylation because the process is based on the second catalytic cycle.

Meanwhile, in 2002, Song and co-workers reported the utilization of porous resins bearing vinyl groups as solid supports, that is, Amberlite XAD-4 (polystyrene-based) or XAD-7 (polyacrylate-based).[21] These resins were treated with OsO_4 in *t*-BuOH/H_2O, and the osmium component was anchored to the resins as Os(VI) and Os(IV) glycolates as was confirmed by XPS analysis (Scheme 3). The catalysts (XAD-4-Os and XAD-7-Os) showed high catalytic activity in asymmetric dihydroxylation using $K_3Fe(CN)_6$ cooxidant. Although the gradual loss of activity was observed, only 1 mol% of XAD-4-Os was recycled five times with constant enantioselectivity (Table 9). The same catalyst was later applied to asymmetric aminohydroxylation by the same authors, although leaching of osmium was observed.[22]



Scheme 3. XAD-4-Os and XAD-7-Os

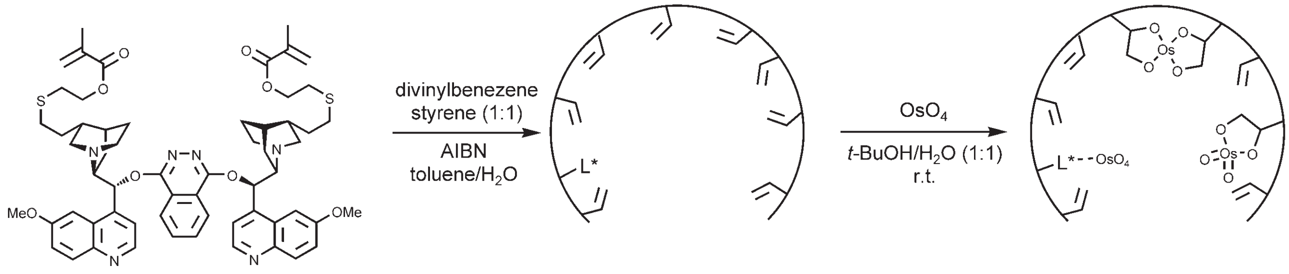
Table 9. Reusability of XAD-4-Os.



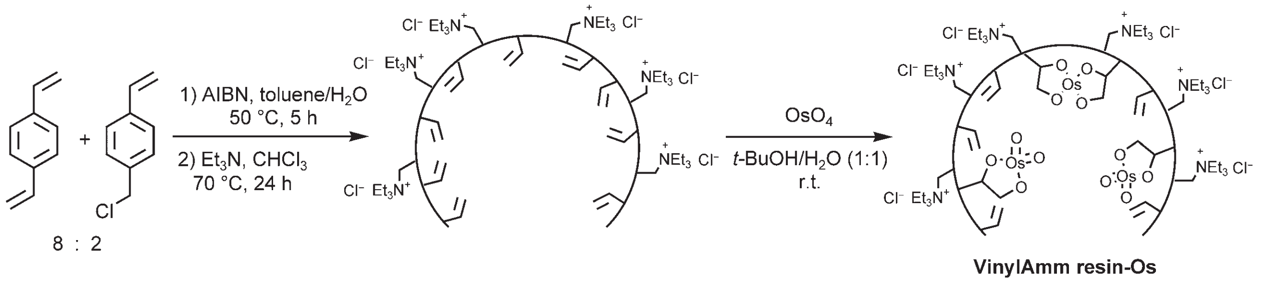
Run	Time [h]	Yield [%]	*ee* [%]
1	2	93	95
2	2	92	95
3	2.5	90	95
4	6	88	95
5	24	88	95

The same group also reported simultaneous immobilization of a chiral ligand and osmium on a vinylated polymer support (Scheme 4).[23] Although good enantioselectivity (90% *ee* for the dihydroxylation of styrene) was observed, leaching of 8–10% of osmium was detected by ICP analysis of the filtrate when the catalyst was reused.

To improve recyclability of the osmium catalyst, the same group introduced both vinyl and quaternary ammonium groups on a polymer support.[24] It is expected that OsO_4 and OsO_4^{2-} are captured by the vinyl and ionic moieties, respectively. The polymer support and the osmium catalyst were prepared according to the reactions shown in Scheme 5. With only



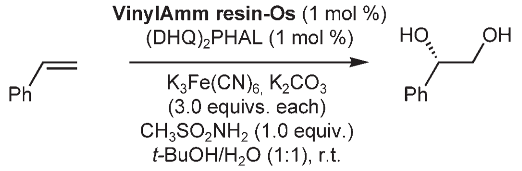
Scheme 4. Simultaneous immobilization of L* and Os.



Scheme 5. Use of a polymer support bearing vinyl groups and quaternary ammonium moieties.

0.2 mol% of the catalyst (VinylAmm resin-Os) and 0.5 mol% of $(DHQ)_2PHAL$, a series of alkenes were transformed to the corresponding diols with high enantioselectivity. Reusability was tested with 1 mol% of the catalyst in the reaction of styrene, showing only slight loss of activity observed in the fifth use (Table 10). Notably, reusability was proved to be very high compared to that of XAD-4-Os[21] and Resin-Os[12].

Table 10. VinylAmm resin-Os catalysts.



Run	Time [h]	Yield [%]	*ee* [%]
1	2	94	95
2	2	91	95
3	2	93	95
4	2	90	95
5	3.5	90	95

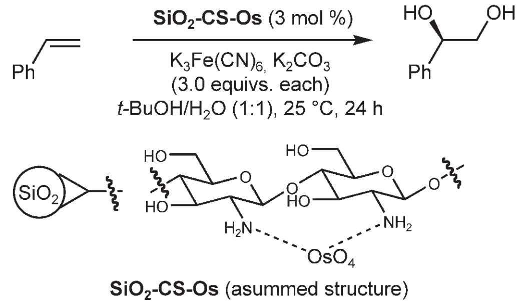
5 Miscellaneous Approaches

Poly(ethylene glycol) (PEG) (Mw = 400) was used as a recyclable reaction medium for asymmetric dihydroxylation.[25] The reaction proceeded rapidly in this medium using only 0.5 mol% of osmium. After each run of the reaction, the product could be extracted with diethyl ether and the PEG layer was repeatedly used without significant loss of activity. The chiral ligand was also recovered to some extent in this medium. The PEG moieties were first introduced in the solid support in PEM-MC Os.[7] Based on the beneficial effect of the PEG media, TentaGel-Os,[16] and $[P/S\text{-}PEG_3][BF_4]$-Os[17] may have similar effects on capturing the osmium component in the supports.

A silica gel-supported chitosan (SiO_2-CS) was utilized for immobilization of osmium and as a chiral ligand.[26] The catalyst (SiO_2-CS-Os) was prepared from this supported chitosan and OsO_4 in the presence of *t*-BuOOH and was used for asymmetric dihydroxylation using $K_3Fe(CN)_6$ as cooxidant in *t*-BuOH/H_2O. SiO_2-CS-Os can be recovered by simple filtration and reused several times without significant loss of activity (Table 11). Similarly, chitin, a poly(*N*-acetylglucosamine), was used as a ligand as well as a support by another group.[27] Although good activity and retention of osmium in the support was observed using NMO as cooxidant, the enantioselectivity was low and catalyst recycling was not successful.

An aqueous solution of a sugar (sucrose) was used as a new, inexpensive immobilization medium in combination with $(QN)_2PHAL$ (tetrahydroxylated *in situ*) for recovery of osmium and the chiral ligand.[28] Although the activity decreased gradually, the catalyst (starting from only 0.1 mol%) was reused three times with constant enantioselectivity without further addition of OsO_4 and the chiral ligand after the first run.

Table 11. SiO2-CC-Os.



Run	Yield [%]	*ee* [%]
1	66	77
2	66	77
3	65	77
4	63	70
5	61	69
6	59	63

6 Perspectives

The development of recoverable and reusable catalysts is of current concern from the viewpoint of environmental preservation as well as resource and cost saving. In this context, realization of truly efficient, immobilized, enantioselective osmium catalysts might be a guidepost of this endeavor, because immobilization of osmium catalysts has many difficulties to be overcome such as toxicity, volatility, contamination in the products, involvement of several oxidation states, reversible coordination of the chiral ligand, etc. This review summarizes recent efforts to address this issue. Although several promising approaches have been revealed, these studies are still underway. More simple and reliable methods are being pursued.

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