Achiral Dihydroxylation of Olefins by Osmate (OsO_4^{2-}) Stabilised on Nanocrystalline Magnesium Oxide

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Abstract: A recoverable and reusable new heterogeneous AP-Mg-OsO_4 catalyst was designed and developed for the first time *via* a counterionic stabilisation of OsO_4^{2-} with Mg^{2+} present on the corner or edge of nanocrystalline MgO. AP-Mg-OsO_4 catalysed the dihydroxylation of olefins to afford diols with excellent yields in the presence of *N*-methylmorpholine *N*-oxide for the first time. The absence of osmium and no progress of the dihydroxylation reaction with the filtrate samples withdrawn periodically during the reaction rule out the leaching of osmium unambiguously and provide evidence for the heterogeneity of the reaction. Identification of surface intermediate species by XPS and TGA-DTA-mass thermography gives an insight into the mechanism of the dihydroxylation reaction.

Keywords: counterionic stabilisation; dihydroxylation; diols; nanocrystalline magnesium oxide; olefins; osmium tetroxide

Osmium-catalysed olefin dihydroxylation, a widely used transformation for the production of vicinal diols, is effected by the well-known Upjohn procedure, while its asymmetric version was developed by Sharpless.[1] However, the high cost, toxicity and possible contamination of osmium catalyst in the products obstructs its wide use in industry. In order to address this problem, Kobayashi et al. reported the immobilisation of osmium in the polymer *via* microencapsulation,[2] Jacobs et al.[3] described the same on silica by covalent anchoring and Yao used the combination of the ionic liquids and 4-(dimethylamino)pyridine for the dihydroxylation of olefins.[4] Recently, we have developed heterogeneous osmium catalysts immobilised on different inorganic[5] and organic[6] solid supports *via* ion exchange, which show the excellent activity in dihydroxylation reactions.

Nanocrystalline metal oxides including MgO, CaO, Al_2O_3 and ZnO have attracted great attention due to their unusual magnetic, optical, physical and surface chemical and catalytic properties.[7–13] These nanoporous materials are mainly used as efficient destructive chemisorbents for toxic gases, NO_2, SO_2, SO_3 and HCl, as well as chlorinated and phosphorus-containing compounds.[8] Nanocrystalline MgO is found to be very active in dehydrohalogenation of chlorohydrocarbons at high temperatures.[9] Due to the high surface area, these nanostructured solid materials exhibit higher activity. The reactivity of these materials is further enhanced by depositing very thin layers of transition metal oxides on the crystallites of MgO.[14] The presence of edge-corner and other defect sites allow the nanostructured MgO materials to possess a high concentration of reactive surface ions. The reactive sites on the surface of MgO are as follows:[15] 1) the Mg^{2+} site which is of the Lewis acid type, 2) the O^{2-} site which is of the Lewis base type, 3) the lattice bound and isolated hydroxy groups and 4) the anionic and cationic vacancies. The presence of corner and edge sites on the surface of AP-MgO could approach 20% while on CP-MgO they amount to less than 0.5% and on CM-MgO essentially to 0%.[16] For example, an edge, or even more so, a corner O^{2-} anion is coordinatively unsaturated and is seeking Lewis acids (electron-deficient species) to help stabilise and delocalise its negative charge. Conversely an Mg^{2+} ion on an edge or corner is seeking Lewis bases (electron-rich species) to stabilise and delocalise its positive charge. Therefore, these coordinatively unsaturated O^{2-} and Mg^{2+} ions readily accept incoming reagents with Lewis acid or Lewis base character. The excess positive charge will always be satisfied with anion deficiency and therefore the structure will not lose its anion exchange capacity during the reaction. The best example is that nano-MgO can absorb up to 13% by weight of Cl^- in the reaction with chlorine gas at room temperature and atmospheric pressure.[17]

This situation presents an opportunity to prepare new and unusual materials, wherein the highly reactive ions could be stabilised by forming adducts with the reactive, accepting surface sites on the MgO. In this communica-

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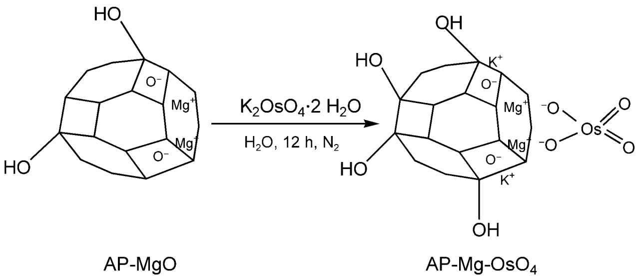


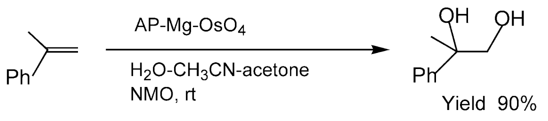
Scheme 1. Preparation of AP-Mg-OsO_4 catalyst.

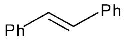
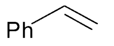
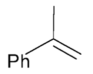
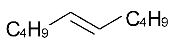
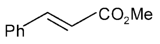
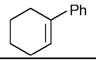
tion we report the novel design and development of the recoverable and reusable new heterogeneous AP-Mg-OsO_4 catalyst obtained *via* counterionic stabilisation of OsO_4^{2-} with Mg^{2+} present on the corner or edge sites of nanocrystalline MgO (Scheme 1) for the dihydroxylation of olefins to afford diols with excellent yields in the presence of *N*-methylmorpholine *N*-oxide (NMO) for the first time. We also describe the identification of surface intermediate species by XPS and TGA-DTA-MS which gives an insight into the mechanism of the dihydroxylation reaction.

In an effort to obtain counterionic stabilisation of OsO_4^{2-} with the Mg^{2+} of the MgO, commercially available CM-MgO [surface area (SA) 30 m^2/g], conventionally prepared CP-MgO (SA 250) and aerogel prepared AP-MgO (SA 390) were treated with K_2OsO_4 to afford the samples of Mg-OsO_4 with SAs of 25, 240, and 340 m^2/g, respectively. In the reaction with AP-MgO, (SA 390) the entire amount of K_2OsO_4 used was consumed. During the preparation of the catalyst, the surface of AP-MgO was hydroxylated as indicated by non-H-bonded OH groups at 3715 cm^{-1} in the IR spectrum. This is consistent with the reactive profile of AP-MgO with water.[18] On the other hand, a small amount ($< 0.3\%$) of osmate was detected in the treated samples of CM-MgO and CP-MgO. When we performed the dihydroxylation of α-methylstyrene using Mg-OsO_4 catalysts, nano-AP-Mg-OsO_4 (SA 340) catalyst was found to be far superior over CP-Mg-OsO_4 (SA 240) using NMO as an oxidant, which is in consonance with the increased content of osmium possible by the presence of the large amount of Mg^{2+} ions. The osmium catalyst prepared from nano-AP-MgO (SA 600) displayed almost the same activity in the dihydroxylation reactions (Table 1, entry 3).

In an effort to understand the scope and application of the osmium catalyst, we tested the achiral dihydroxylation of various olefins, including aromatic, aliphatic, acyclic, cyclic, mono- and disubstituted olefins, to afford diols in high yields. First we carried out dihydroxylation of α-methylstyrene (1 mmol) in a mixture of H_2O-CH_3CN-acetone (1:1:1, 6 mL) using nano-AP-Mg-OsO_4 (SA 340, 2 mol %), NMO (1.3 mmol). The reaction was performed at room temperature to obtain the diols in high yields (Table 1).

Table 1. Dihydroxylation of olefins with AP-Mg-OsO_4



Entry	Olefin	Isolated yield [%][a]
1		94 (90,89,87,85)[b]
2		93
3		90, (87)[c] (5)[d] (89,87,88,86)[b]
4		85
5		96 (95,93,94,92)[b]
6		90

[a] The yields are obtained with AP-Mg-OsO_4 (SA 340).

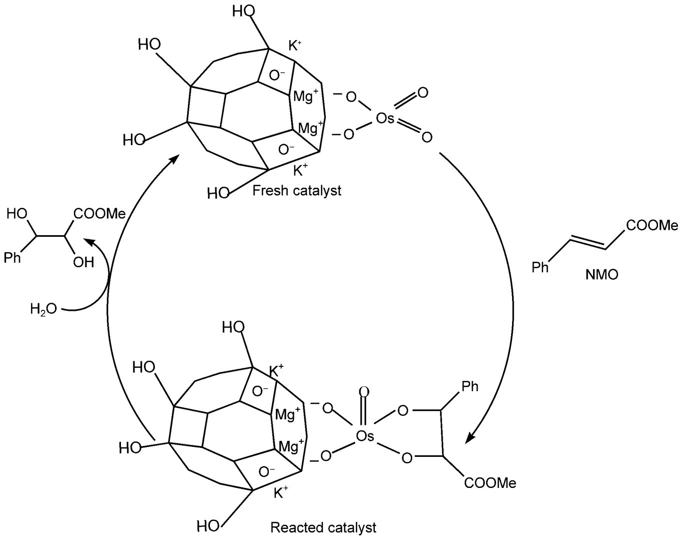
[b] The yield obtained in the 2nd, 3rd, 4th and 5th cycles.

[c] Isolated yield obtained with osmium catalyst prepared from AP- MgO(SA 600).

[d] Yield with Mg-OsO_4 (SA 240) after 24 h.

The heterogeneous dihydroxylation of olefins by nanocrystalline AP-Mg-OsO_4 was performed in H_2O-CH_3CN-acetone (1:1:1) using NMO as the cooxidant. The scope of AP-Mg-OsO_4 catalyst was extended successfully for the hydroxylation of relatively larger substrates, e.g., stilbene (Table 1, entry 1) and methyl cinnamate (Table 1, entry 5). This is interesting to note that the microencapsulated catalyst by Kobayashi was never reported for the dihydroxylation of the above substrates with NMO as cooxidant. Furthermore, in the case of *trans*-5-decene the yield is 85% as against 77% obtained using the Kobayshi catalyst.[2a]

The AP-Mg-OsO_4 was recovered quantitatively by simple filtration. The recovered catalyst was reused and consistent activity was noticed even after the fifth cycle (Table 1, entries 1, 3 and 5). When the fresh reaction was conducted with the filtrate obtained at the end of the dihydroxylation reaction, no product formation was observed. Moreover, the absence of osmium as determined by iodometry, SEM EDX and no progress of dihydroxylation reaction with the filtrate samples withdrawn periodically during reaction rules out the leaching of osmium unambiguously and provides evidence for heterogeneity throughout the reaction (see Experimental Section for further details). It is interesting to note that the AP-MgO 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 AP-Mg-OsO_4 is



Scheme 2. Proposed mechanism for the AP-Mg-OsO$_4$-catalysed dihydroxylation of olefins.

treated with the oxidant in the absence of olefin, osmium is found to leach from the support, which indicates that the AP-Mg-OsO$_4$ catalyst is not stable in the oxidative environment.

To provide further evidence for the heterogeneity and understand the mechanism, an intermediate species on the solid catalyst, Mg-OsO$_4$R was synthesised by reaction with NMO-olefin (methyl cinnamate) (Scheme 2) in dry acetone and identified. The experiment was conducted separately under anhydrous conditions and the mixture was washed thoroughly with a small amount of water, followed by acetone to remove the adhered species. In the XPS of fresh Mg-OsO$_4$R, Os 4f$_{7/2,5/2}$ lines appear at 54.8, 57.4 and 54.4, 57.1 eV, respectively, which indicate Os is in the +VI oxidation state (see the Supporting Information). The XPS of the Mg-OsO$_4$R carbon 1 s resolved on curve fitting shows two lines at 285.0 and 289.4 eV. The higher binding energy line is ascribed to a C–O bond presumably of an Os-glycolate complex on the surface, which is indeed confirmed by TGA-DTA-mass thermogram. The *m/z* values 162, 90, 103, 77, and 59 amu (See the Supporting Information) observed are assigned to radical cations of Ph-CH-CH-COOMe, PhCH, COOMe fragmented from the complexed glycolate on the Mg-OsO$_4$R as depicted in the Scheme 2. No *m/z* value corresponding to the diol is observed to strengthen that these fragments are really obtained in the Os-glycolate complexes bound to the support. On hydrolysis of Mg-OsO$_4$R by treating it with water at room temperature, the diol was obtained as indicated by HPLC, which indeed provides confirmation of the formation of an Os-glycolate intermediate on the heterogeneous support. Thus, these studies unambiguously establish the heterogeneity of the reaction and give insight into the mechanism for achiral dihydroxylation.

In summary, we have shown that the new reusable and recoverable heterogeneous AP-Mg-OsO$_4$ catalyst developed here is active for the dihydroxylation of olefins. For the first time we are able to trap an Os-glycolate complex on the solid state which gives insight into the mechanism of the dihydroxylation of olefins. Further work on the asymmetric dihydroxylation of olefins is in progress.

Experimental Section

Preparation and Characterization of the Mg-OsO$_4$ Catalysts

Commercially available CM-MgO [surface area (SA) 30 m^2/g, 1 g], conventionally prepared CP-MgO (SA 250, 1 g) and aerogel prepared AP-MgO (SA 390, 1 g) were treated with K$_2$OsO$_4$ (0.184 g, 0.5 mmol) dissolved in decarbonated water under stirring for 12 h under a nitrogen atmosphere to afford the samples of Mg-OsO$_4$ with the SAs of 25, 240, and 340 m^2/g, respectively. Then the catalyst was filtered off and washed with deionised water, acetone, and dried.

The catalyst AP-Mg-OsO$_4$ (340) is well characterised by FTIR, UV-DRS, SEM and XPS. The FTIR spectra of AP-Mg-OsO$_4$ showed a broad absorption band centred at 815–820 cm^{-1}, which is assigned to the vibrational asymmetric O=Os=O stretching, unlike the sharp bands observed at 819 cm^{-1} in case of potassium osmate. The observation of broad bands in the same region indicates that the OsO$_4^{2-}$ is unaffected during formation of adduct with the Mg^{2+} on the support, while experiencing very weak interactions with the support. The UV/Vis diffuse reflectance spectra of the AP-Mg-OsO$_4$ catalyst shows an identical pattern to that of potassium osmate dihydrate, with the absorption maxima at 295 nm, which indicates that the octahedral coordination of Os(VI) composed of two water molecules is unperturbed upon exchange. The SEM-EDX of AP-Mg-OsO$_4$ shows the presence of 8.96% osmium. The IR and XRD of the AP-Mg-OsO$_4$ samples indicated that the surface of the support was hydroxylated.

Typical Procedure for Dihydroxylation of Olefins with AP-Mg-OsO$_4$ (SA 340) using NMO as the Cooxidant

An olefin (1 mmol), AP-Mg-OsO$_4$ (46 mg, 2 mol % of Os) and NMO (1.3 mmol) were placed in a round-bottomed flask containing H$_2$O-CH$_3$CN-acetone (1:1:1, 6 mL) and stirred for 8–10 h at room temperature (except entries 5, 6 for 20 h, Table 1). After completion of the reaction (checked by TLC), the AP-Mg-OsO$_4$ catalyst was filtered and washed with methanol. After removing the solvent, the crude material was chromatographed on silica gel to afford the corresponding *cis*-diol.

Heterogeneity Tests

We evaluated the heterogeneity of the catalyst in all respects. We conducted three different dihydroxylation experiments to obtain clear evidence for the heterogeneity of the reaction.

Experiment 1: A mixture of AP-Mg-OsO_4, α-methylstyrene and NMO in H_2O-CH_3CN-acetone was stirred for 8 h. After completion of the reaction, the catalyst was separated by filtration. To one part of the filtrate were added fresh α-methylstyrene, NMO and the mixture was stirred for 24 h. There was no enhancement in the yield of the product. To the second part of the solution were added a different olefin (*trans*-stilbene), NMO and the mixture was stirred for 24 h. No stilbene diol was formed.

Experiment 2: A mixture of AP-Mg-OsO_4, α-methylstyrene and NMO in H_2O-CH_3CN-acetone was stirred at room temperature. At different intervals (for every 2 h) the samples were withdrawn and filtered. To these filtrates were added a different olefin (*trans*-stilbene), NMO and the mixture was stirred for 24 h. No stilbene diol was formed. Furthermore, no osmium was detected in the filtrates by the SEM-EDX.

From the above experiments it was observed that no osmium was leached during or at the end of the reaction when all the constituents were present. It is, therefore, concluded that the OsO_4 is bound to the support during the reaction. It appears that during oxidation with NMO the anionic form of OsO_4 is transformed into an Os(VIII) species, but is bound to the support through some other electrostatic interaction that includes hydrogen bonds with the Brønsted hydroxyl groups of MgO.

Experiment 3: A mixture of AP-Mg-OsO_4 and NMO in H_2O-CH_3CN-acetone was stirred for 24 h at room temperature and filtered. To the filtrate was added α-methylstyrene and the mixture was stirred for 8 h. The diol was formed in good yield.

The result clearly shows that the catalyst suffers from leaching of osmium upon treatment with the cooxidant in the absence of the olefin.

Iodometry Test

The absence of osmium in the filtrate is further reconfirmed using the iodometry test.[2a] The iodometry test was performed as follows: after treatment of the catalyst in the H_2O-CH_3CN-acetone (1:1:1) solvent system, the catalyst was filtered and the filtrate was treated with potassium iodide and HCl. The solution was titrated with sodium thiosulphate in the presence of starch, and no formation of iodine was observed.

SEM-EDX Procedure

The samples were completely dried for scanning electron microscopy. The dried samples were mounted on aluminium stubs using double adhesive tape, coated with gold in a HUS-5GB vacuum evaporator and scanned in a Hitachi S-520 Scanning Electron Microscope with a Link ISIS-300, Oxford EDAX Detector.

Supporting Information Available

Figure S1. XPS (survey scan) data of fresh catalyst. Figure S2. TGA-DTA-Mass thermogram of $MgOsO_4R$ ($MgOsO_4$ interacted with olefin).

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