Supplementary Information

Markedly enhanced recyclability of osmium catalyst in asymmetric dihydroxylation reactions by using macroporous resins bearing both residual vinyl groups and quaternary ammonium moieties

Kwang Jin Kim,[a] Han Young Choi,[a] Soon Ho Hwang,[a] Yil Sung Park,[a,]* Eun Kyung Kwueon,[b] Doo Seong Choi[b] and Choong Eui Song[b,]*

[a] *DongWoo Fine-Chem Co., Ltd, 1177, Wonjung-ri, Poseung-myeon, Pyeongtaek-si, Gyeonggi-do 451-820 Korea*
[b] *Institute of Basic Science, Department of Chemistry, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon-si, Gyeonggi-do, 440-746, Korea, E-mail: s1673@skku.edu*

General Procedures

IR spectra were recorded on a AVATAR 320 FT-IR spectrometer. Diffuse reflectance UV spectra (UV-DRS) were recorded on a Varian CARY 2200 spectrophotometer. X-ray photoelectron spectroscopy(XPS) was performed by AES-XPS, ESCA2000. The NMR spectra were recorded on a Varian Unity Inova 300MHZ spectrometer. HPLC (High Performance Liquid Chromatography) for the determination of enantiomeric purity was performed by Varian prostar 321 UV/VIS apparatus. Column chromatography was performed using Kieselgel 60 (230~400 mesh) and TLC was carried out using glass sheets pre-coated with silica gel 60F_{254} purchased from Merck.

OsO_4 was purchased from Next Chimica, South Africa. All of olefins, $K_2OsO_4{\cdot}2H_2O$, $(DHQ)_2PHAL$, $K_3Fe(CN)_6$ and $CH_3SO_2NH_2$ were purchased from Aldrich. All other solvents and chemicals were obtained from commercial sources, and were used without further purification.

Preparation of macroporous chloromethylated resin 1

A mixture of hydroxypropyl methyl cellulose (400 mg) and NaCl (22.0 g) with H_2O (350 mL) was stirred at 40 °C for 30 min. To this solution, divinylbenzene (60.9 g, 468 mmol) and vinylbenzyl chloride (17.9 g, 117 mmol), AIBN (0.8 g, 6.8 mmol) and toluene (80 mL) were added, and the resulting solution was stirred for 40 min at 40 ^{o}C and additionally stirred for 6 h at 80 ^{o}C. The produced copolymer **1** was filtered and washed thoroughly with H_2O, methanol and acetone. The macroporous copolymer **1** was then transferred to a Soxhlet thimble and extracted for 24 h using acetone to remove any soluble impurities. Finally the resin **1** was dried at 40 ^{o}C under vacuum. The Cl-analysis indicated that 0.91 mmol/g of vinyl benzylchloride were incorporated in the resin **1**. The content of active vinyl groups in the resin **1** was also determined by mercury acetate titration method (0.63 mmol/g of vinyl group).

Preparation of *VinylAmm* resin

Triethylamine (2 mL, 14.3 mmol) and chloroform (15 mL) were charged into the resin **1** (1 g), and stirred for 24 h at 70 ^{o}C. The produced macroporous resin ***VinylAmm*** bearing both residual vinyl groups and ammonium moiety was filtered and washed thoroughly with H_2O, methanol and acetone. The ***VinylAmm*** resin was then transferred to a Soxhlet thimble and extracted for 24 h using acetone to remove any soluble impurities. Finally the ***VinylAmm*** resin was dried at 40 ^{o}C under vacuum. Nitrogen analysis of the ***VinylAmm*** resin indicated that 0.50 mmol/g of quaternary ammonium moiety were incorporated. The content of active vinyl groups in the resin 1 was also determined by mercury acetate titration method (0.28 mmol/g of vinyl group).

Preparation of the resin supported osmium catalyst, *VinylAmm* resin -OsO_4

To the mixture of ***VinylAmm*** resin (1.008 g) in *t*-BuOH/H_2O (v/v) 1:1, 10 mL), 1 wt % of aqueous solution of OsO_4 (5 mL, 0.040 mmol of Os/mL) was added at room temperature. The reaction mixture was stirred for 24 h at room temperature. During the reaction of the resins with OsO_4, the solid turned black, while no color developed in the solution. The supported osmium catalyst was filtered, and the filtered resin was then washed with methanol several times and dried in vacuo for 24 h. UV analysis of the filtrate indicated that all OsO_4 used was anchored to the resins (0.18 mmol of Os per gram of resin). Nearly no trace amounts of osmium could be found in filtrates. These result was revalidated by XRF (X-ray Fluorescence Spectrometer) analysis of resins.

Characterization of Catalyst, *VinylAmm resin* -OsO_4

Diffuse reflectance UV/vis spectrum: The diffuse reflectance UV/vis spectra of the resin-OsO_4 show the absorption maximum in the range of 310-320 nm (**Figure 1**).[1]

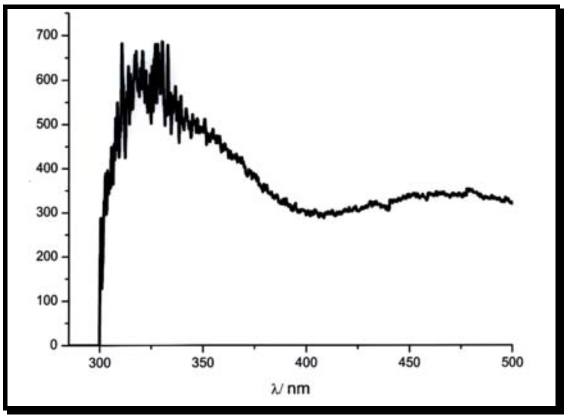
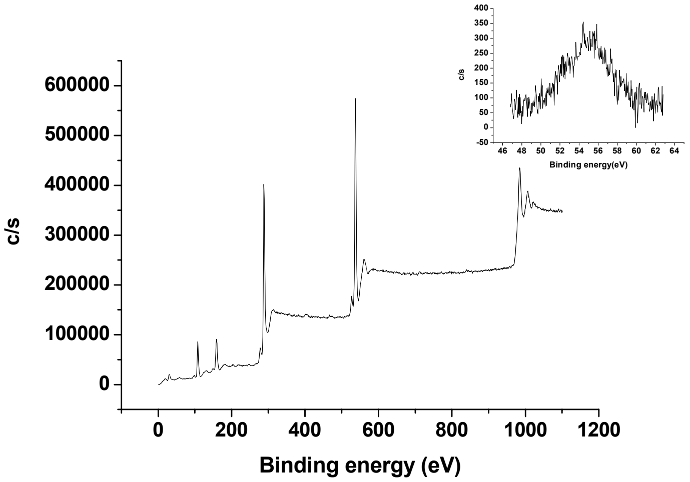
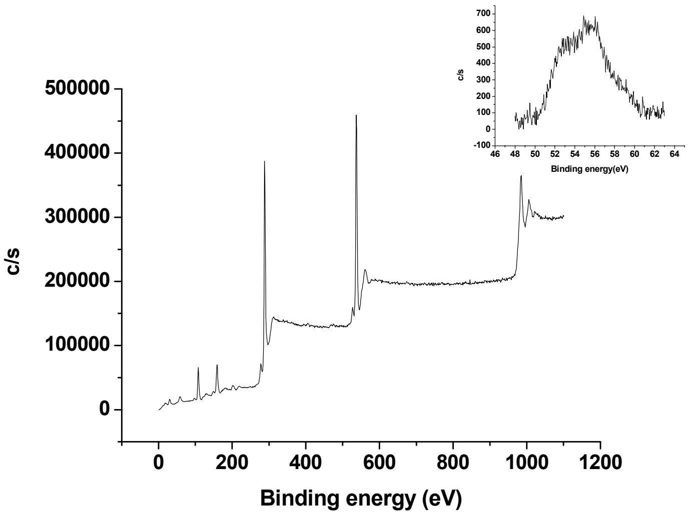


Figure 1. Diffuse reflectance UV/vis spectra of the resin-OsO_4

XPS spectra of the *VinylAmm*-OsO_4 complex: In the XPS (X-ray Photoelectron Spectroscopy) spectra of the resins, Os $4f_{7/2}$ lines appeared at ~53 eV and ~50 eV (inset of **Figure 2.b**)[2] Based on these values, it is clear that the osmium tetroxide is reduced to Os(VI) monoglycolate and Os(IV) bisglycolate in the reaction with vinyl groups of resins.



a. before use



b. after reaction

Figure 2. XPS spectra of the *VinylAmm*-OsO_4 complex (a, before use; b, recovered after reaction)

Preparation of *MerrAm*m resin:

The *MerrAmm* resin was prepared by quaternisation of triethylamine (2.2 mL, 21 mmol) with 1 g of chloromethylated styrene-divinylbenzene copolymer (1% cross-linked Merrifield resin, capacity ~2.1 mequiv/g) according to the procedure reported by Choudary et al.[3]

Experimental procedure for the asymmetric dihydroxylation of olefins:

A mixture of a solid osmium catalyst (e.g. ***VinylAmm*** resin, 0.18 mmol/g, 0.03 mmol), which is filled in a commercially available small cylindrical container with mesh wall (MicroKanTM), $(DHQ)_2PHAL$ (0.03 mmol), $K_3Fe(CN)_6$ (9 mmol), K_2CO_3 (9 mmol), $CH_3SO_2NH_2$ (3 mmol) and olefin (3 mmol) in *t*-BuOH-H_2O (v/v = 1:1, 15 mL) was stirred at room temperature. After completion of the reaction, the catalyst was filtered and subsequently washed with *t*-BuOH-H_2O (v/v = 1:1). Saturated aqueous sodium sulfite and 1N HCl were added to the filtrate and the mixture was stirred for an additional hour. Organic product was extracted with ethyl acetate. After removing the solvent, the crude product was purified by chromatography on silica gel with EtOAc/hexanes affording *cis*-diol.

Reuse of catalysts. The reusability of resin-OsO_4 catalyst was carried out by performing the AD of Styrene on a 3 mmol scale. After completion of the reaction, the catalyst was recovered by filtration and subsequently washed with ethyl acetate and dried. The recovered resins were reused for successive reactions. The chiral ligand of $(DHQ)_2PHAL$ was recovered (>95%) from the aqueous layer by usual acid-base work up.

Charaterization of Products: The following compounds are known compounds, and their NMR 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. HPLC (Chiralcel OD-H, *i*-PrOH/hexane (v/v = 5:95), flow rate 0.5 mL min^{-1}): t_R = 31.6 min (*R*-isomer), t_R = 34.8 min (*S*-isomer).

1-Phenyl-1,2-propanediol. HPLC (Chiralcel OD, *i*-PrOH/hexane (v/v = 4.5:95.5), flow rate 0.75 mL min^{-1}): t_R = 20.8 min (*R*,*R*-isomer), t_R = 22.0 min (*S*,*S*-isomer).

1-Phenyl-1,2-cyclohexanediol. HPLC (Chiralcel OJ, *i*-PrOH/hexane (v/v = 8:92), flow rate 1.0 mL min^{-1}): t_R = 11.2 (*S,S*-isomer), t_R = 14.6 (*R,R*-isomer).

1,2-Diphenyl-1,2-ethanediol. HPLC (Chiralcel OJ, *i*-PrOH/hexane (v/v = 10:90), flow rate 1.0 mL min^{-1}): t_R = 14.8 min (*S*,*S*-isomer), t_R = 17.8 min (*R*,*R*-isomer).

Methyl 2,3-dihydroxy-3-phenylpropionate. HPLC (Chiralcel OJ, *i*-PrOH/hexane (v/v = 20:80), flow rate 1.0 mL min^{-1}): t_R = 11.0 min (2*R*,3*S*-isomer), t_R = 14.3 min (2*S*,3*R*-isomer).

References

1. Choudary, B. M.; Chowdari, N. S.; Kantam, M. L.; Raghavan, K. V. *J. Am. Chem. Soc.* **2001**, *123*, 9220.
2. (a) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomden, K. D. *Handbook of X-ray Photoelectron Spectroscopy,* Perkin-Elmer Corp., **1992**. (b) Severeyns, A.; De Vos, D. E.; Fiermans, L.; Verpoort, F.; Groet, P. J.; Jacobs, P. A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 586.
3. (*a*) B. M. Choudary, N. S. Chowdari, M. L. Kantam and K. V. Raghavan, *J. Am. Chem. Soc*., 2001, **123**, 9220; (*b*) B. M. Choudary, N. S. Chowdari, K. Jyothi and M. L. Kantam, *J. Am. Chem. Soc.,* 2002, **124**, 5341.