Supporting Information

Osmium Replica of Mesoporous Silicate MCM-48: Efficient and Reusable Catalyst for Oxidative Cleavage and Dihydroxylation Reactions

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A. Preparation of 3-D networked Os nano-material (N-Os):^a A Pyrex glass ampoule (1×7 cm, wall thickness = 2 mm) containing C₁₆-MCM-48¹ (0.2 g) and Os₃(CO)₁₂ (0.75 g; Strem, 99%) was evacuated by a diffusion pump for 1 h, and then flame-sealed. The ampoule was heated at 265 °C in a furnace. The color change of MCM-48 from white to brown indicated efficient sorption of brown liquid produced by the melting of thermolysis products of Os₃(CO)₁₂, such as Os₅C(CO)₁₅, Os₆(CO)₁₈, and Os₇(CO)₂₁.² In order to induce decomposition of the Os cluster compounds into Os metal, the ampoule was heated at 265 °C for 3 days, further heated at 350 °C for 6 h, and finally maintained at 400 °C for 24 h. The ampoule was carefully broken (**CAUTION! The ampoule was cooled in liquid N₂ before breakage, since the pressure build-up from liberated CO was very high.**), and the black-colored powder thus obtained was treated by H₂ (100 mL/min) at 400 °C for 6 h, which resulted in complete removal of the carbon contents (Elemental Analysis; C, 0.0 %). After subsequent thermal annealing at 550 °C under Ar for 12 h, the furnace was cooled down to room temperature, and the Os@MCM-48 sample was exposed to air. In order to obtain template-free Os nanomaterial (N-Os), the resulting black powder was reacted with 48 % HF in H₂O (20 molar excess based on Si content) at room temperature (**CAUTION! Use an efficient fume hood with a special care to avoid skin-contacts of HF solution.**). Centrifugation and drying under vacuum gave voluminous black powder (0.45 g). The prepared nano-material was characterized by XRD (Rigaku D/MAX-RC (12 kW) diffractometer using graphite-monochromatized Cu-K α radiation at 40 kV and 45 mA), TEM (Philips F20Tecnai operated at 200 kV), XPS (VG scientific ESCALAB 200R, Al K α), and BET N₂ adsorption isotherms (Micromeritics ASAP 2400, 77K).

XPS spectra of *N*-Os

^a When Os₃(CO)₁₂ was heated in a vacuum sealed ampoule without added MCM-48, only thick mirror of osmium metal resulted, which is highly adherent to the wall of the ampoule. This indicates that the addition of MCM-48 is imperative for the formation of 3-D networked osmium nano-material. The formed osmium mirror does not show any catalytic activity toward reactions described in the manuscript.

B. Catalysis

Materials and instrumentation. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 400 FT (400 and 100 MHz, respectively) spectrometer. Chemical shift are reported in delta (δ) units, parts for million (ppm) downfield from tetramethylsilane, or in ppm relative to the singlet at 7.26 ppm of chloroform-*d*₁. Splitting patterns are designated as follows: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, td; triple of doublet, dd; double of doublet, tt; triple of triplet, b; broad. IR spectra were recorded with a BIO-RAD FTS 165 Spectrometer. Column chromatography was carried out using silica gel 60 (230-400 mesh, ASTM) (Merck). Commercially available solvents were purified by standard procedures. All substrates including alkenes and alkynes except benzyl (5-hexynyl) ether (Table 1, entry 11) were purchased from Fluka Co. and Aldrich Co., and were used as obtained without further purification. Oxone and 4-methylmorpholine *N*-oxide (NMO) were purchased from a commercial supplier and were used as obtained. Inductively Coupled Plasma (ICP) was taken using a Perkin Elmer Optima 4300DU spectrometer.

Preparation of benzyl (5-hexynyl) ether (Table 1, entry 11): To a solution of 5-hexyn-1-ol (500 mg, 5.1 mmol) in THF (20 mL) was added potassium hydride (204 mg, 5.1 mmol) at 0 °C and the mixture was stirred for 5 min at room temperature followed by addition of benzyl bromide (915 mg, 5.4 mmol) and tetrabutylammonium iodide (19 mg, 0.05 mmol). The reaction mixture was stirred for 2 h at room temperature, quenched with water (10 mL), extracted with ethyl acetate, dried over anhydrous MgSO₄, and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:15) to afford analytically pure product (845 mg, 88 %): ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.25 (5H, m), 4.51 (2H, s), 3.50 (2H, t, *J* = 6.1 Hz), 2.23 (2H, td, *J* = 7.0, 2.7 Hz), 1.95 (1H, t, *J* = 2.4 Hz), 1.76-1.62 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 138.5, 128.3, 127.6, 127.5, 84.3, 72.9, 69.7, 68.4, 28.7, 25.2, 18.2; IR (neat) 3297, 2948, 2870, 1716, 1453, 1317, 1277, 1118, 714 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₆O [*M*⁺] 188.1202, found 188.1207.

Representative Procedure for the Oxidative Cleavage:^b To a solution of 4-bromostyrene (80 mg, 0.437 mmol) in DMF (0.9 ml) were added *N*-Os catalyst (4.2 mg, 0.022 mmol) and then Oxone (1.07 g, 1.75 mmol). The mixture was stirred for 2 h at room temperature. After completion of the reaction, which was confirmed by TLC, the reaction mixture was quenched with water (10 mL) and the solution was diluted with ethyl acetate (20 ml). The organic layer was dried over anhydrous MgSO₄, filtered, and then concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:3) to afford analytically pure 4-bromobenzoic acid (72.0 mg, 82.0 %).

^b Solubilities in DMF are poor for both excess Oxone and side-products, which are derived from the Oxone oxidant after the oxidation reaction, making the recovery of pure *N*-Os particles difficult under the employed conditions.

Spectroscopic data of 3-benzyloxy-3-phenyl propanoic acid (Table 1, entry 6): ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.24 (10H, m), 4.86 (1H, m), 4.48-4.30 (2H, m), 2.92-2.70 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 176.5, 140.3, 137.8, 130.2, 128.5, 128.3, 128.2, 127.8, 127.7, 126.7, 77.4, 70.7, 43.3; IR (neat) 3032, 1713, 1454, 1310, 1285, 1095, 699 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₆H₁₆O₃ [*M*⁺] 256.1100, found 256.1101.

Representative Procedure for the Dihydroxylation Reaction: To a solution of 4-

methymorpholine *N*-oxide (102 mg, 0.87 mmol, 1.2 equiv) in water/acetone (0.7/0.3 mL) was added a suspension of *N*-Os (6.9 mg, 0.036 mmol, 0.05 equiv) in *t*BuOH (0.5 mL) and then the mixture was stirred for 30 min at room temperature. To the above solution was added slowly *trans*-stilbene (132 mg, 0.73 mmol) and the reaction mixture was stirred for additional 4 h at room temperature. Sodium hydrosulfate (200mg) and water (15ml) was added to the mixture and pH of this solution was adjusted to 2 using 1N H₂SO₄ solution. The solution was saturated with NaCl and stirred for 30 min and then aqueous phase was extracted with ethyl acetate (12 mL x 3). The organic phase was dried (MgSO₄) and concentrated under reduced pressure to give a crude diol, which was further purified by silica gel column chromatography (ethyl acetate/hexane = 1:10) to afford hydrobenzoin (142 mg, 91%).

Representative Procedure for Recovery and Reuse of the Nano-Osmium Catalyst:^c

To a solution of 4-methymorpholine *N*-oxide (253 mg, 2.2 mmol) in water/acetone (1.5/0.6 mL) was added a suspension of *N*-Os (17 mg, 0.089 mmol, 0.05 equiv) in *t*BuOH (1 mL). The mixture was stirred for 30 min at room temperature. To the above mixture was added α -methylstyrene (213 mg, 1.8 mmol) and the reaction mixture was stirred at room temperature. After completion of the reaction (4 h), ethyl acetate (13 mL) was added into the reaction vessel and the mixture was centrifuged for 2 h to give a precipitate of Os nanomaterial. The precipitate was washed with ethanol (15 mL x 3) and dried under reduced pressure to afford the Os nanomaterial (17 mg), which was reused without further purification.

TEM image of the recovered *N*-Os

^c As mentioned in text (Reference number 17), the ICP analysis of the filtrate after the reaction showed that Os contents were less than <5 ppm in each recycled run of dihydroxylation of Table 2. This led us to test a dihydroxylation reaction of α -methylstyrene with 0.03 mol % of OsO₄ (the maximum amount of possibly leached out osmium, if any) under otherwise identical conditions as in Table 2. In the control experiment with OsO₄, much slower and incomplete conversion (61%), even after a much longer reaction time (24 h), was observed.

[1] Ryoo, R.; Joo, S. H.; Kim, J. M. *J. Phys. Chem. B* **1999**, *103*, 7435.

[2] Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Matheson, T. *J. Organomet. Chem.* **1973**, *57*, C82.