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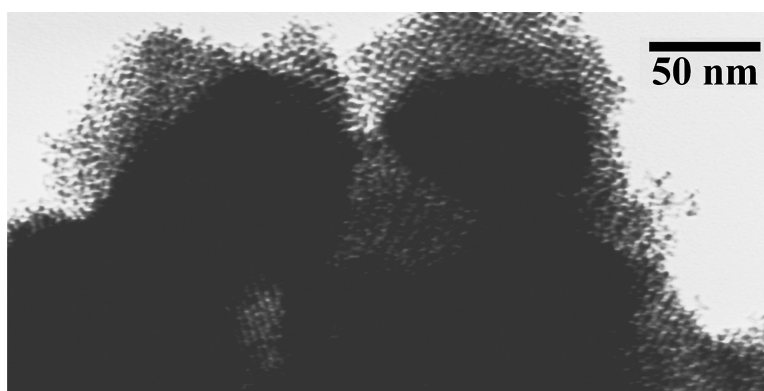
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Osmium Replica of Mesoporous Silicate MCM-48: Efficient and Reusable Catalyst for Oxidative Cleavage and Dihydroxylation Reactions

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Nanostructured materials have received considerable attention because of their novel size- and shape-dependent electronic, magnetic, optical, and catalytic properties that differ drastically from those of bulk materials,[1] and current research efforts are focused on the preparation of nanomaterials with new morphologies.[2] Metals with designed three-dimensional (3-D) nanostructures, in particular, are expected to find useful applications in catalysis.[3] Recently, replication of mesoporous silicate templates by thermal vapor infiltration or solution-phase infiltration techniques has led to the formation of 3-D networks of nanosized Pd[4] and Pt.[5] The tedious experimental procedures and rather low incorporated metal contents (6−30 wt % of SiO_2 weight), however, make their applications impractical.

The Os-catalyzed organic transformations such as dihydroxylation and oxidative cleavage of olefins are highly versatile synthetic methods for the preparation of key intermediates in organic synthesis.[6] High volatility and toxicity of Os components in the homogeneous catalysis, however, severely limit their large-scale application. Although several approaches have been reported to immobilize OsO_4,[7] it is still highly desirable to develop an easily handled and recyclable Os catalyst system with high catalytic activity comparable to that of OsO_4 and preferably with lower toxicity. Herein, we report a highly efficient replication of MCM-48 to give a 3-D networked osmium nanomaterial and its superior heterogeneous catalytic activity in oxidative cleavage and dihydroxylation.

A Pyrex glass ampule containing MCM-48 (0.2 g) and $Os_3(CO)_{12}$ (0.75 g) was evacuated and then flame-sealed. To induce decomposition of $Os_3(CO)_{12}$ into Os metal, the ampule was heated in a furnace at 265 °C for 3 days,[8] further heated at 350 °C for 6 h, and finally maintained at 400 °C for 24 h. The ampule was broken (*CAUTION!*),[9] and the obtained black powder was treated with H_2 at 400 °C for 6 h to remove carbon impurities. After subsequent thermal annealing at 550 °C under Ar, the furnace was cooled to room temperature. To remove the SiO_2-based template, the resulting black powder was treated with aqueous 48% HF (*CAUTION!*).[10] Repeated washing with methanol, centrifugation, and drying under vacuum gave a voluminous black powder (0.45 g, 225 wt % of SiO_2 weight).[11]

The X-ray powder diffraction (XRD) pattern (Rigaku D/MAX-RC (12 kW), Cu Kα, 40 kV, 45 mA, 25 °C) of the black powder shows broad peaks at 43°, 69°, 78°, and 84°, which correspond to (101), (110), (103), and (112) reflections of nanostructured *hcp*-Os (JCPDS card no: 06-0662), respectively (Figure 1). It also shows a low angle peak at $2\theta = 2.2°$, suggesting that the black powder retains some degree of long-range order transferred from the MCM-48 host. Such a long-range ordered structure is further supported by transmission electron microscopy (TEM, Philips F20Tecnai operated at 200 kV) studies. The TEM images of the black powder
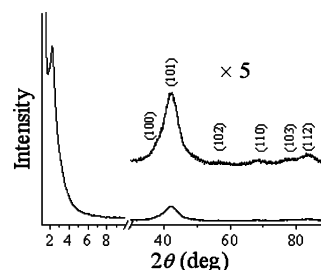

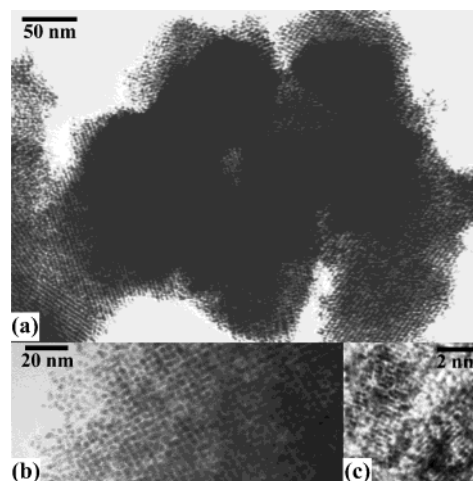**Figure 1.** XRD pattern of *N*-Os.

Figure 2. TEM micrographs of *N*-Os at various magnifications.

(Figure 2a,b) show a substructure of 3-D networked Os nanoparticles with a diameter of ∼3 nm. The high-resolution TEM image in Figure 2c shows the lattice fringe images (*d* spacing = 2.37 Å) from the (100) plane of highly crystalline Os. A very high BET surface area (126 m^2/g) has been obtained for the 3-D networked Os nanomaterial (*N*-Os) from N_2 adsorption isotherms.

Triggered by recent reports on the direct cleavage of olefins into carboxylic acids using OsO_4 catalyst,[12] oxidative cleavage of unsaturated compounds by *N*-Os was scrutinized. Various substrates were smoothly converted to the corresponding carboxylic acids in high yields within a few hours at room temperature in the presence of stoichiometric oxidant (Oxone) and *N*-Os catalyst (0.05 equiv) (Table 1). While Oxone was most efficient among the various oxidants tested, no reaction was observed in the absence of *N*-Os catalyst. As demonstrated in entries 1−5, the efficiency of the catalyst is little affected by substituents with different electronic properties. Cleavage of *trans*-stilbene produced 2 equiv of benzoic acid in good yield (entry 8), and 1,1-disubstituted olefin afforded the corresponding ketone (entry 9). It is particularly noteworthy that alkynes were also cleaved to carboxylic acids, which has never

Table 1. Oxidative Cleavage of Alkenes (Alkynes) with Oxone in the Presence of N-Os Catalyst[a]

$$R\diagdown\!\!\diagup (R\!-\!\!\equiv) + \text{Oxone} + N\text{-Os} \xrightarrow[25\ ^\circ\text{C}]{\text{DMF}} R\!-\!CO_2H$$

entry	olefin (alkyne)		time (h)	yield (%)[b]
1		R = H	2	83
2		^{t}Bu	2	78
3		Br	2	82
4		OAc	3	75
5		NO$_2$	5	89
6	Ph (OBn)		5	66
7	Ph		2	97
8	Ph—Ph		3	91[c]
9	Ph		2	99[d]
10	Ph—≡		15	92
11	BnO(CH$_2$)$_5$—≡		15	65
12	Ph—≡—CH$_2$CH$_3$		15	84[e]

[a] Reactions were carried out with a substrate (1 equiv), Oxone (4 equiv), and N-Os (0.05 equiv). [b] Isolated yield by column chromatography. [c] Based on 2 equiv of benzoic acid. [d] Acetophenone. [e] Benzoic acid.

Table 2. Dihydroxylation of Alkenes in the Presence of N-Os Catalyst[a]

entry	olefin	time (h)	yield (%)[b]
1	1-hexene	2	81
2	styrene	3	99
3	*trans*-stilbene	4	88
4	cyclohexene	2	89
5	indene	4	78
6	1-methylcyclohexene	4	89
7	α-methylstyrene (1st run)	4	91
8	α-methylstyrene (2nd run)	4	90
9	α-methylstyrene (3rd run)	4	87
10	α-methylstyrene (4th run)	4	92
11	α-methylstyrene (5th run)	4	82

[a] All reactions were performed with olefin (1 equiv), 4-methylmorpholine N-oxide (1.2 equiv), and N-Os (0.05 equiv) in acetone/water/^{t}BuOH at 25 °C. [b] Purified yield by column chromatography.

been reported to the best of our knowledge, although it took a little longer to get satisfactory yields (entries 10−12). As suggested by Borhan,[12b] the oxidative catalytic cleavage of alkenes seems to proceed via aldehyde rather than 1,2-diol intermediacy.[13] However, use of less oxidant did not guarantee the preferential formation of aldehydes. For example, reaction of benzyl alcohol with 1.0 equiv of Oxone in the presence of N-Os catalyst (0.05 equiv) gave benzaldehyde only in 30−40% yield with comparable formation of benzoic acid under a variety of conditions.[14] In contrast, use of NaIO$_4$ as an oxidant (2 equiv) in aqueous dioxane gave benzaldehyde in 90% yield.[15]

Dihydroxylation of alkenes into vicinal diols is another prominent example where OsO$_4$ has displayed an excellent catalytic activity. Under Upjohn conditions, diverse types of alkenes were oxidized to the corresponding 1,2-diols in good yields in the presence of N-Os catalyst without overoxidation of the diol products (Table 2). It was found that N-Os could be quantitatively recovered by a simple workup procedure after reaction.[16] A TEM image showed that the integrity of the recovered osmium particle was not changed during the reaction. The recovered N-Os could be recycled several times without much loss of catalytic activity (entries 7−11). In each

run, the N-Os was recovered quantitatively by centrifugation, and inductively coupled plasma (ICP) analysis of the filtrate showed that leaching of Os from the matrix was negligible during the recycles.[17] Further studies on detailed mechanistic pathways, especially regarding substructures of osmium during the oxygen transfer steps, are in progress.

In summary, we have shown an efficient preparative protocol of 3-D networked osmium nanomaterial by utilizing the capillary action of mesopores of MCM-48 toward molten organometallic precursors as well as its high catalytic activity[18] and excellent reusability in certain oxidation reactions. We believe that other 3-D networked nanostructured metals could also be prepared by a similar method and further related studies would undoubtedly produce various nanocatalysts with novel catalytic activities.

Supporting Information Available: Preparation and characterization details for the Os nanomaterial and experimental details of catalytic reactions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) At 265 °C, Os$_3$(CO)$_{12}$ decomposes to form a brown liquid containing Os$_5$C-(CO)$_{15}$, Os$_6$(CO)$_{18}$, and Os$_7$(CO)$_{21}$, which easily enters mesopores of MCM-48 via a capillary action.

(9) The ampule was cooled in liquid N$_2$ before breakage, because the pressure buildup from liberated CO was very high.

(10) Use an efficient fume hood with a special care to avoid skin contact.

(11) The X-ray photoelectron spectroscopy (XPS) of the black powder shows peaks due to Os and O, indicating surface oxidation of the Os nanomaterial, but no discernible osmium oxide phase is observed either in the TEM or in XRD analysis. See Supporting Information.

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(13) While aldehydes reacted readily to give carboxylic acids in good yields under the reaction conditions, no conversion was detected with 1,2-diols.

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(16) See Supporting Information for detailed experimental procedure.

(17) ICP analysis of the filtrate showed that Os contents were less than <5 ppm in each run.

(18) No catalytic conversion was observed for the oxidative cleavage and dihydroxylation reactions with commercially available Os powder under otherwise identical conditions.

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