A Structurally Simple supported Metal Catalyst Prepared from Decaosmium Carbonyl Clusters on Magnesium Oxide

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$[Os_{10}C(CO)_{24}]^{2-}$ on MgO was used to prepare supported metal clusters that are inferred from EXAFS spectroscopy to retain the nuclearity of ten during catalysis of n-butane hydrogenolysis.

Elucidation of relations between structure and properties of supported metal catalysts has been slow, hindered by the lack of catalysts incorporating metal aggregates (clusters) of a single size and shape. Earlier attempts to prepare such catalysts using molecular metal clusters as precursors[1,2] failed because key requirements, isolated surface-bound clusters and a cluster core resistant to oxidative fragmentation during activation, were not met. Typically, Al_2O_3-supported catalysts were prepared from low-nuclearity clusters [*e.g.*, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$]; these precursors broke up on heating in inert atmospheres or air and, upon subsequent exposure to H_2, produced distributions of clusters with nuclearities much larger than the original.

The precursor $[Os_{10}C(CO)_{24}]^{2-}$ (**1**) was synthesized on the basic MgO surface by reductive carbonylation of Os^{IV} species, as described previously.[3] IR spectra and quantitative extraction of surface-bound anions indicated that the yield of surface-bound (**1**) was about 90%. Analysis of the Os L_{III} extended *X*-ray absorption fine structure (EXAFS) of (**1**) on MgO (Figure 1), using the difference-file technique[4] and multiple-shell fitting in *k* space, yielded first-shell co-ordination parameters in excellent agreement with both the crystallographic data for $[Ph_2PN^+]_2[(\mathbf{1})]$[5] and co-ordination parameters derived from EXAFS spectroscopy of microcrystalline $[Et_4N^+]_2[(\mathbf{1})]$ (Table 1). Transmission electron microscopy (TEM) of (**1**) on MgO gave evidence of only uniform

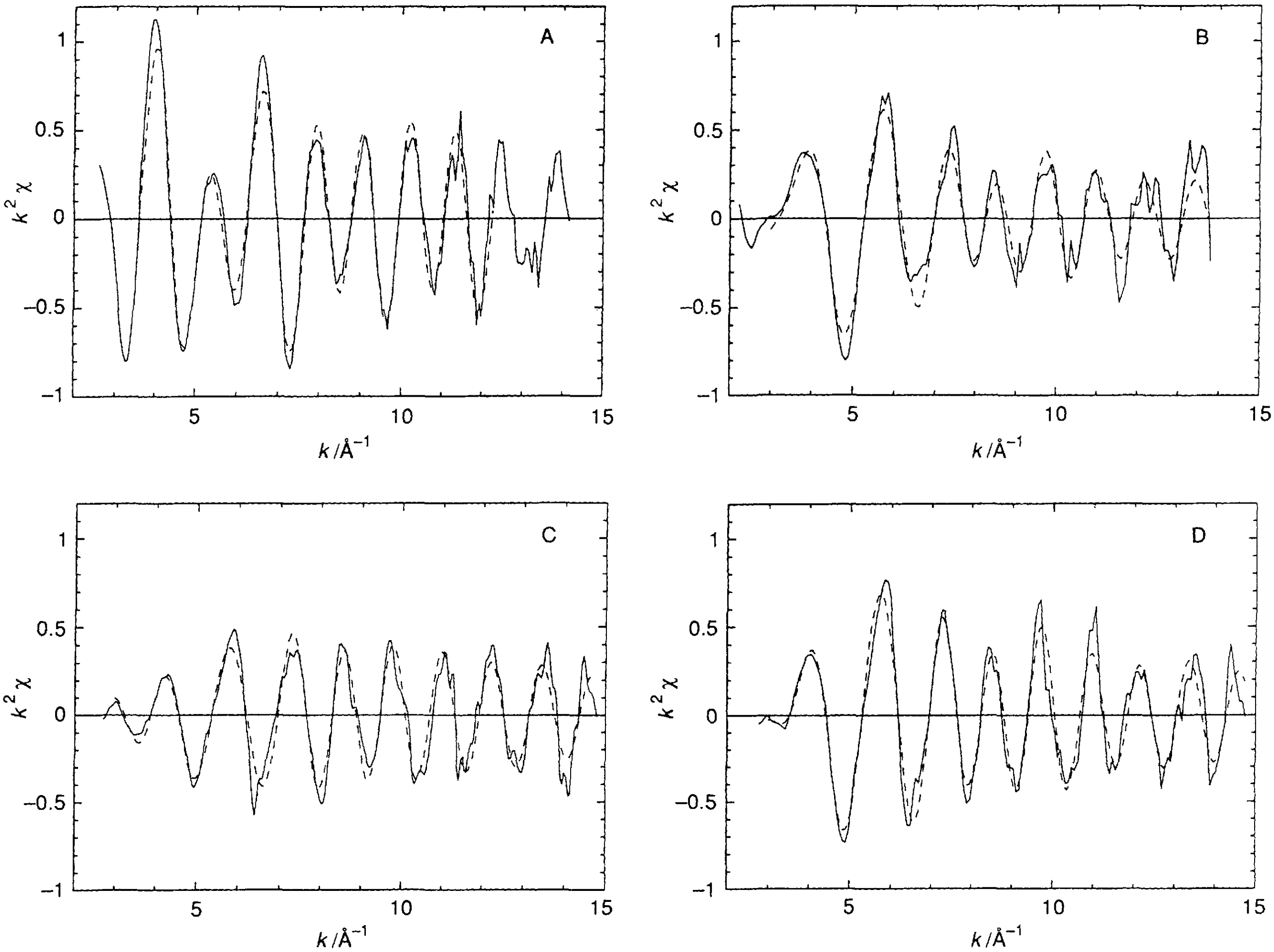

Figure 1. Experimental (——) and calculated best fit (---) Os L_{III} EXAFS of supported decaosmium (k^2 weighted): $[Os_{10}C(CO)_{24}]^{2-}$ on MgO (A), after decarbonylation in He at 573 K (B), after subsequent treatment in H_2 at 573 K (C), and after catalysis of n-butane hydrogenolysis at 523 K (D).

Table 1. First-shell co-ordination parameters derived from OsL_{III} EXAFS.

Sample	Backscatterer	N^a	R /Å^b	$10^3\Delta\sigma^2$ /Å^{2c}	ΔE_0 /eV^c
$[Et_4N]_2[Os_{10}C(CO)_{24}]$ crystals mixed with boron nitride	Os	4.8	2.86	2.4	1.0
	C	0.6	2.04	−4.3	0.0
	C	2.4	1.88	1.3	0.0
	O	2.4	3.04	1.0	0.0
$[Os_{10}C(CO)_{24}]^{2-}$/MgO	Os	4.8	2.86	2.8	1.2
	C	0.6	2.02	−6.5	0.0
	C	2.4	1.86	−1.2	0.0
	O	2.4	3.03	−0.8	0.0
Surface species resulting from decarbonylation of $[Os_{10}C(CO)_{24}]^{2-}$/MgO	Os	3.8	2.67	3.7	1.2
	O and/or C	2.9	2.03	7.3	1.9
	$O_{support}$	2.0^d	2.64	1.6	−1.0
Supported clusters resulting from subsequent H_2 treatment	Os	4.7	2.67	3.4	−1.3
	O and/or C	0.8	2.09	5.6	−0.7
	$O_{support}$	1.8^d	2.63	0.5	−2.4
Supported clusters after catalysis of n-butane hydrogenolysis	Os	5.0	2.68	3.3	0.9
	O and/or C	2.2	2.04	5.7	0.4
	$O_{support}$	2.1^d	2.62	−0.4	−1.3

[a] Co-ordination number (approximate uncertainty of estimate): N_{Os-Os} (±15%), N_{Os-C} (±15%), N_{Os-O} (±15%), and $N_{Os-Osupport}$ (±30%). [b] Interatomic distance (approximate uncertainty of estimate): R_{Os-Os} (±0.02 Å), R_{Os-C} (±0.03 Å), R_{Os-O} (±0.03 Å), $R_{Os-Osupport}$ (±0.03 Å). [c] Debye–Waller factors ($\Delta\sigma^2$) and inner potential corrections (ΔE_0) are relative to the reference compounds Re powder (Os–Os), $Na_2Pt(OH)_6$ (Os–O, Os–C, and Os–$O_{support}$), and $Os_3(CO)_{12}$ [Os–C and Os–O contributions in (**1**)]. [d] Os–$O_{support}$ co-ordination numbers were adjusted to account for the differences in metal–oxygen interatomic distances between the samples and the reference compound; the expression $N = N_{fit}/\{\exp[-2(R - R_{ref})/\lambda]\}$ with λ (the electron mean free path) set equal to 6 Å was used.

high-contrast scattering centres ≈10 Å in size, consistent with isolated decaosmium clusters.

Temperature-programmed decomposition (TPDE) of (**1**) on MgO in flowing He indicated the evolution of *ca.* 15 molecules of CO per cluster between 523 and 653 K; a sharp maximum in CO evolution was observed at 598 K, consistent with the decomposition of uniform surface species. CO_2 (*ca.* 4 molecules per cluster), H_2, and CH_4 also were evolved. After TPDE, approximately 6 C atoms remained per 10 Os atoms. *In situ* IR spectroscopy gave no evidence of partially decarbonylated surface species, such as the mononuclear Os^{II} subcarbonyls that result from oxidative fragmentation of triosmium carbonyl clusters on Al_2O_3[5,6] and MgO.[7]

The Os L_{III} EXAFS spectrum measured after heating (**1**) on MgO in He at 573 K for 2 h (Figure 1) indicates the presence of both Os and low-Z backscatterers. The Os–Os contribution obtained from fitting (Table 1) is consistent with groupings of 5—6 *metallic* Os atoms (R_{Os-Os} = 2.67 Å), possibly the remnants of the Os_6C core of (**1**). This hypothesis is consistent with the solution chemistry of (**1**); the octahedral core, stabilized by an interstitial C ligand, is highly resistant to fragmentation, but Os–Os bonds between capping $Os(CO)_3$ groups and the core are severed by electrophiles such as NO^+ and I^+.[8] The low-Z EXAFS shell at 2.03 Å is strongly disordered, suggesting a mixture of covalently bound C and O backscatterers. A second low-Z contribution at 2.64 Å is associated tentatively with O atoms of the Os^0–MgO interface.[9] The present EXAFS analysis and TPDE data cast doubt on the proposal[10] that (**1**) on γ-Al_2O_3 can be partially decarbonylated and retain the tetracapped octahedral structure of the molecular cluster. We suggest that this sample, derived from heating (**1**) on γ-Al_2O_3 in He at 523 K,[10] contained a mixture of intact molecular clusters and fully decarbonylated surface species, thus biasing the EXAFS results.

The decarbonylated sample derived from (**1**) on MgO was exposed to flowing H_2 at 573 K for 1 h to remove O and C ligands. The measured EXAFS spectrum (Figure 1) is dominated by Os backscattering. Most significant, the Os–Os co-ordination number obtained from fitting (Table 1) is equivalent to that of the precursor (**1**), suggesting the presence of metallic decaosmium clusters on the support. Apparently any Os atoms lost to oxidative fragmentation during decarbonylation remained nearby on the support, as observed in the decomposition of $HOs_3(CO)_{10}\{OAl\}$ to form ensembles of three $Os(CO)_2$ or $3\{OAl\}_2$ species;[11] we infer that H_2 treatment resulted in the reduction and reincorporation of these vicinal Os atoms into the metallic clusters. Low-Z backscatterers were observed, consistent with the expected EXAFS contribution of the Os^0–MgO interface.[9] This contribution was fitted satisfactorily by an Os–$O_{support}$ shell; the estimated co-ordination number suggests a structural model having *ca.* 5 Os atoms per cluster in contact with the MgO surface. The remaining low-Z contribution is attributed to residual C ligands.[12]

In contrast to the decaosmium carbonyl (**1**) on MgO, samples formed by decarbonylation and H_2 treatment were catalytically active for n-butane hydrogenolysis, a standard test reaction. The catalyst was formed from (**1**) on MgO by treatment in a microflow reactor as described above and then subjected to a flow of n-butane, H_2, and He with a 1:10:9 molar ratio at 1 bar. The steady-state reaction rate with the decaosmium catalyst was 0.28 mmol of n-butane (g of Os)$^{-1}$ s^{-1} at 500 K, less than half that measured with a conventional Os/MgO catalyst prepared by H_2 reduction of H_2OsCl_6 on MgO. The latter catalyst consisted of supported Os aggregates 10—30 Å in size, as evidenced by EXAFS spectroscopy (N_{Os-Os} = 8.1) and TEM. The difference in activity of the two catalysts confirms the structure sensitivity of n-butane hydrogenolysis.[13]

After the catalyst had functioned for 10 h at 523 K in the flow reactor, it was examined by EXAFS spectroscopy. The spectrum indicated that the first-shell Os–Os co-ordination number (Table 1) was equivalent within experimental uncertainty to that found after initial exposure of the catalyst to H_2, consistent with an unchanged nuclearity of the Os clusters on the MgO support. Qualitative comparison of the higher-shell EXAFS contributions of the fresh and used catalysts showed no significant differences. The EXAFS of the used catalyst also contains a dominant low-*Z* contribution at 2.04 Å (Table 1) that we suggest arose from carbonaceous deposits formed on the surface during operation. The $Os–O_{support}$ contribution remained essentially unchanged, consistent with maintenance of the cluster structure during catalysis.

In summary, an n-butane hydrogenolysis catalyst formed from (**1**) on MgO was inferred on the basis of EXAFS spectroscopy to have retained the nuclearity of ten, the first supported metal catalyst with this degree of structural uniqueness.

We thank D. C. Koningsberger and D. E. Sayers for helpful discussions and the staffs of the National Synchrotron Light Source, Brookhaven National Laboratory (USA) and the Synchrotron Radiation Source, Daresbury Laboratory (UK). This work was supported by the National Science Foundation (CBT 8605699 and CTS-8910633).

Received, 20th March 1990; Com. 0/01231I

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