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EXAFS STUDIES OF OXIDE SUPPORTED OSMIUM CARBONYL CLUSTERS

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Résumé. Les réactions des complexes triosmiums sur les silices modifiées à surface spécifique importante ont été étudiées en utilisant l'EXAFS du seuil du Os L(III). La réaction de $[Os_3(CO)_{12}]$ avec $HS(CH_2)_3SIL$ conduit à la formation de $HOS_3(CO)_{10}[S(CH_2)_3SIL]$ dont la structure a été analysée par la méthode des ondes sphérique en ce qui concerne l'étude de l'EXAFS. La décomposition sous vide a donné une nouvelle matière. La coordination était approximativement de deux groupes carbonyles, deux atomes d'oxygène, un atome de soufre et deux atomes d'osmium; on a proposé une structure trinucléaire avec ces nombres de coordination. Le premier produit résultant de la réaction de $[H_2Os_3(CO)_{10}]$ avec $PPh_2C_2H_4SIL$ était un produit d'addition de ces groupements. Sa décomposition a donné une espèce partiellement décarbonylée semblable à celle qui était obtenue sur $HS(CH_2)_3SIL$ mais la différence était l'absence de coordination au ligand original. La coordination aux deux atomes d'oxygène de surface a accompagné la décarbonylation thermique.

Abstract. The reactions of triosmium carbonyl clusters on functionalised high surface area silicas have been monitored by Os L(III) edge EXAFS. Interaction of $[Os_3(CO)_{12}]$ with $HS(CH_2)_3SIL$ affords $HOS_3(CO)_{10}[S(CH_2)_3SIL]$, which was structurally characterised using spherical wave methods to analyse the EXAFS data. Subsequent thermolysis *in vacuo* yields a new material. Coordination to ~ 2 CO groups, ~ 2 oxygen atoms, ~ 1 sulphur and ~ 2 osmium atoms is evident; a trinuclear structure is consistent with these coordination numbers. The initial product of the interaction of $[H_2Os_3(CO)_{10}]$ with phosphinated silica is a phosphine adduct of this cluster. Subsequent thermolysis yields a partially decarbonylated species similar to that formed on the thiolated silica with the exception of the absence of coordination to the original anchoring ligand. Coordination to surface oxygen accompanies thermal decarbonylation.

1. Introduction

As part of a programme to synthesise new well-defined heterogeneous catalysts starting from organometallic complexes, we have employed Os L(III) edge EXAFS to monitor the chemistry of osmium carbonyl clusters on the surface of ligand functionalised sil-type silicas. Two materials are compared. Firstly, interaction of triosmium dodecacarbonyl with a thiolated silica, $HS(CH_2)_3SIL$, has been shown by IR studies to yield $HOS_3(CO)_{10}(SC_3H_6SIL)$ (1) [1]. The bridging thiolate ligand apparently stabilises the tethered complex, since thermal decomposition is much slower than that of $H_2Os_3(CO)_{10}(PPh_2C_2H_4SIL)$ (2); the latter material acts as an alkene hydrogenation catalyst until deactivated by this decomposition [2]. The EXAFS study is aimed at establishing the nature of these decompositions.

2. Experimental

The Os L(III) edge X-ray absorption spectra were recorded in transmission mode on Line 7 of the Synchrotron Radiation Source at the SERC Daresbury Laboratory. The procedures used for data reduction and analysis by spherical wave methods have been outlined previously [3].

3. Results and Discussion

Four spectra of the tethered complex (1) were averaged to provide the data set used for the analysis. The fit obtained on an initial 3 shell model incorporating the Os neighbours and the CO ligands was improved by the inclusion of sulphur shell from the bridging thiolate. The parameters thus obtained were similar to those derived for the model complex $H_2Os_3(CO)_{10}(SPr-n)$ (3). On complex (3) the major discrepancy from expected interatomic distances was for the carbonyl oxygens ($\sim 0.1 \text{ \AA}$). This is an artefact arising from the phase shifts employed for this shell which were modifications to simulate the multiple-scattering contributions to the total back-scattering. The structure for this supported complex is presented in Figure 1.

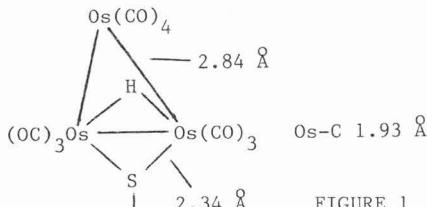


FIGURE 1 EXAFS derived structural details for (1).

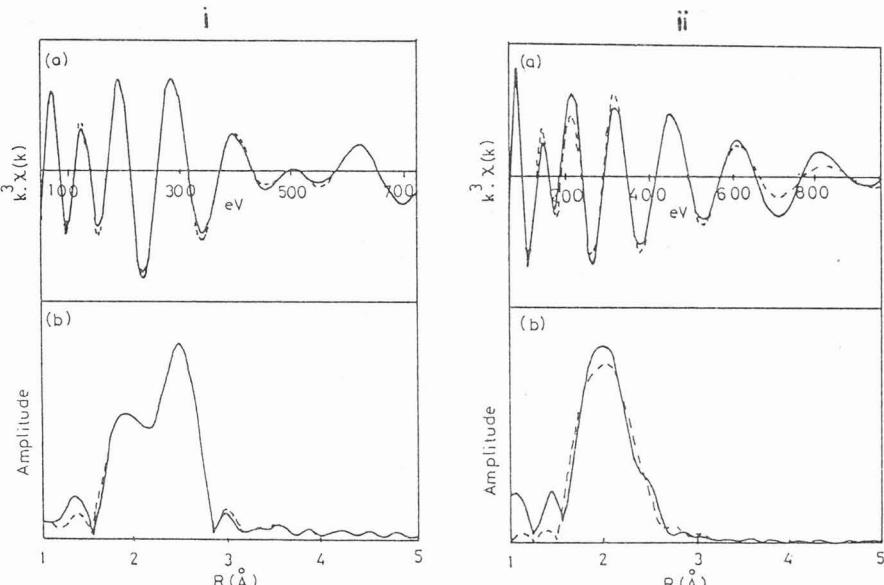


FIGURE 2 Calculated (---) and Fourier filtered experimental plots (—) of (a) $k^3 \cdot \chi(k)$ against photoelectron energy (eV) and (b) their Fourier transforms, corrected for carbon phase shifts, against shell radius (\AA). Data for the inner shell components of the Os L(III) edge EXAFS of (i) the material (4) and (ii) material (5).

Thermal decomposition of (1) and (2) was complete after 24–48 h at 140°C. These new materials (4) (thiolated silica) and (5) (phosphinated silica) both exhibit 3 broad terminal C–O stretching vibrations which provide little structural information. The Os L(III) edge EXAFS data was analysed initially in two Fourier filtered regions in R-space (Figure 2). The inner region for material (4), i.e. 0.99–2.37 Å (no phase shift correction) could only be fitted with 3 components of carbon, sulphur and oxygen. In contrast, Fourier filtered data on a similar region for material (5) only required 2 components, carbon and oxygen, to achieve a satisfactory fit. No significant improvement was obtained when a phosphorus shell was included in the model. Analysis of the outer shell region (~2.2–~3.1 Å apparent shell radius) in each case indicated the presence of oxygen and osmium back-scatterers.

For both these systems the analysis was repeated using data Fourier filtered over the entire evident R-space range, and the results of this analysis are presented in Table 1. Again, any attempt to include a phosphorus shell to fit the data on the material (5) on phosphinated silica only yielded ill-defined parameters. In contrast, the sulphur shell coordination shell on (4) appears to be well-defined. This can be illustrated by contour maps of the fit index for a grid of values of two correlated variables [4]. A comparison of 2 such maps is given as Figure 3. In the first of these, values of the shell radius and coordination number are linked. There is a well defined minimum in this case. A higher degree of correlation would be anticipated between the coordination number and the Debye Waller factor, but although the minimum is less well defined here, nevertheless the coordination number estimate of 1.0 appears to be firm.

Shell	(4)		(5)	
	ON	Radius (Å)	ON	Radius (Å)
C	2.2(3)	1.899(5)	1.6(1)	1.860(2)
O	1.8(4)	2.27(8)	1.9(2)	2.233(2)
S	1.0(1)	2.41(1)	—	—
Os	1.8(7)	2.84(2)	2.2(3)	2.816(4)
O	1.0(4)	2.90(1)	1.1(2)	2.867(5)

TABLE 1 Optimum fits for the Os L(III) edge EXAFS of (4) and (5) (ON = occupation number).

There are two possible structural models which can provide a connexity in osmium of 2 viz linear chains or triangular. A plausible structural model based on the latter option is shown in Figure 4. In both (4) and (5) the coordination centres contain ~2 CO groups and ~2 oxygen atoms, perhaps bridging in nature. On thiolated silica, the site X would be principally sulphur. This may be as inorganic sulphide, since dealkylation of the thiolate group has been observed in derivatives of (1) [5]. However on material (5), this site X is largely vacant. Recent solid state P-31 nmr studies on (5) are consistent with the phosphine having dissociated from the complex, although the small coordination shifts observed in these complexes prevent this from being diagnostic [6].

This represents a difficult situation for EXAFS, since the information provided by other spectroscopic techniques on these pyrolysed samples was limited to indicating the presence of terminal carbonyl groups. Coordination to oxygen, the soft donor atom of the surface functionalisation and neighbouring metal atoms had not been established by any other technique. This work demonstrates that providing the analysis procedures are checked with some similar model compounds and due notice is taken of the reliability of the derived parameters that EXAFS can be extremely valuable in the study of metal sites on the surface of high area oxides.

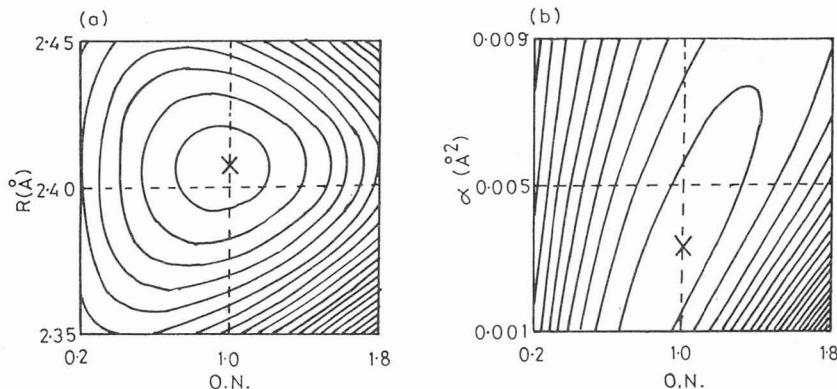


FIGURE 3 Contour maps of the fit index for the correlations for the sulphur shell of material (4). (a) shell occupation number (ON) v shell radius (R), minimum 0.17 at ON 1.0, R 2.41 \AA , lower contour 0.50, increment 0.67, upper contour 13.17. (b) ON v Debye Waller, α , minimum 0.17 at ON 1.0, α 0.003 \AA^2 , lower contour 0.35, increment 0.38, upper contour 7.53.

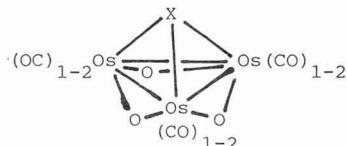


FIGURE 4 Possible structures for the metal species of (4) and (5). (4) $X = S$, (5) $X = \text{CH}_3$ or vacant.

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