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EXAFS SPECTROSCOPY OF SUPPORTED OSMIUM CLUSTERS

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EXAFS spectroscopy has been used to investigate the stability of small osmium clusters at low concentration (ca. 1 wt %) at oxide and sulphide surfaces under conditions of interest in catalyst preparation. Two conditions have been investigated: (a) after impregnation of the osmium cluster compound onto the oxide or sulphide support, (b) after generation of catalytic activity by thermal activation. Three situations are reported: in the first, a 10-metal-atom cluster survived both impregnation onto alumina and activation without change of nuclearity; in the second, a 6-metal-atom cluster survived impregnation onto cadmium sulphide, but dissociated on activation; in the third, the same 6-metal-atom cluster reacted with alumina on impregnation with change of configuration. The ability of EXAFS spectroscopy to provide information regarding structural changes in the active phase of such a catalyst has been demonstrated.

There is currently much interest in the use of metal cluster compounds as precursors in the preparation of supported metal catalysts, in the expectation that it will be possible in the future to prepare metal catalysts having sites of known size and geometry which confer high activity and selectivity. For progress to be made in this area it is necessary to explore the chemistry of metal cluster compounds at support surfaces. We have studied the interactions of the 10-metal-atom cluster $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ with alumina and of the 6-metal-atom cluster $\text{Os}_6(\text{CO})_{18}$ with alumina and with cadmium sulphide. The first-mentioned cluster in the pure state has metal atoms in a tetracapped octahedral configuration (I) whereas the second has a bicapped tetrahedral configuration (II) (Figure 1). We have studied these materials from the standpoint of preparation, chemical characterisation, chemisorption properties, and catalytic activity ([1-4] and papers in preparation); this paper reports some structural aspects of the chemistry of these systems.

Samples were prepared by impregnation of the metal cluster carbonyls from organic solvents onto the supports at a loading of about 1% by weight Os. Thermal activation was achieved by heating the impregnated materials in vacuum or in a helium flow from room temperature to 523 K at 10 K min^{-1} . EXAFS spectra were obtained at the Synchrotron Radiation Source (SRS) at the SERC Daresbury Laboratory. The source ran at 2 GeV. Fluorescence detection was used and the activated samples were examined *in situ* in cells with environmental control.

System (i): $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ /alumina. Figure 2 shows the EXAFS spectra of a pure $\text{Os}_{10}\text{C}(\text{CO})_{24}$ salt [5], of $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ impregnated onto alumina, and of the activated catalyst. The spectra are closely similar, and detailed analysis shows that the tetracapped octahedral structure of the 10-metal-atom cluster has been retained throughout with only slight loss of carbonyl ligands providing the catalyst sites; details of the bond distances will be published in reference 4. Thus, this cluster configuration survives both impregnation and thermal activation. It is

noteworthy that the configuration is that of simple close packing in the fcc system (although bulk osmium crystallises in the hcp system).

System (ii): $\text{Os}_6(\text{CO})_{18}$ /cadmium sulphide. Figures 3a and 3b show the Fourier transforms of the spectra of the impregnated material and of the activated material respectively. The former is closely similar to that of the pure compound, from which we conclude that the parent compound has retained its cluster integrity at the cadmium sulphide surface. This is confirmed by the infrared spectrum of the impregnated material, which contains all 16 characteristic bands of the pure material in the range 1900 to 2120 cm^{-1} . However, on thermal activation, a material is formed in which the extent of osmium-osmium bonding is very greatly reduced (Figure 3b), indicating that cluster integrity has been largely lost. This material catalyses reactions which can be achieved at single metal atom sites (e.g. ethene hydrogenation) but does not catalyse reactions requiring sites consisting of an ensemble of metal atoms (e.g. ethane hydrogenolysis).

System (iii): $\text{Os}_6(\text{CO})_{18}$ /alumina. The spectrum of the pure cluster and of the impregnated material are shown in Figure 4a. It is clear that a molecular change has occurred, because the spectrum of the impregnated material differs substantially from that of the pure compound. However, the clustered state has been retained, as evidenced by the strong contribution of the direct osmium-osmium bonding component at 0.283 nm in the Fourier transform (Figure 4b). Full analysis shows that there has been chemical reaction with the alumina leading to the formation of both osmium-aluminium and osmium-oxygen bonds, and that the osmium cluster structure has partially unfolded as shown in Figure 5.

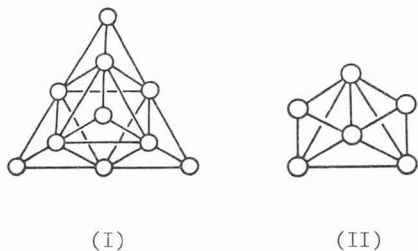


FIGURE 1. Metal atom configurations for starting materials $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ (I) and $\text{Os}_6(\text{CO})_{18}$ (II).

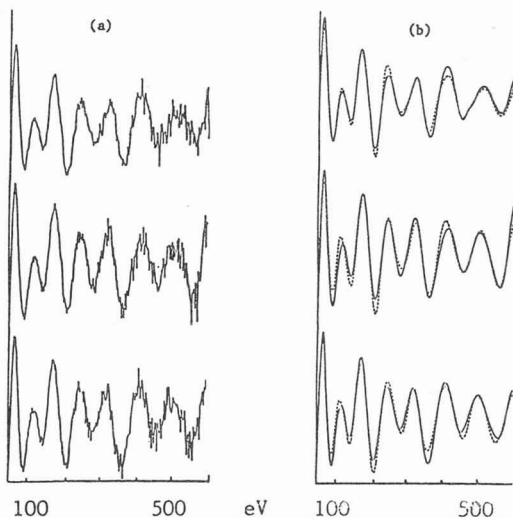


FIGURE 2. (a) EXAFS spectra of an $\text{Os}_{10}\text{C}(\text{CO})_{24}$ salt (upper), impregnated $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ /alumina (centre) and activated $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ /alumina (lower), (b) Full curves are smoothed versions of (a); dashed curves represent theoretical spectra based on the retention of the tetracapped octahedral configuration of the cluster. Spectra are K^2 weighted.

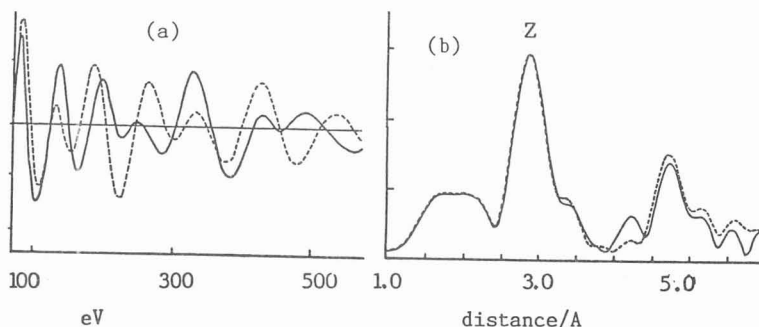
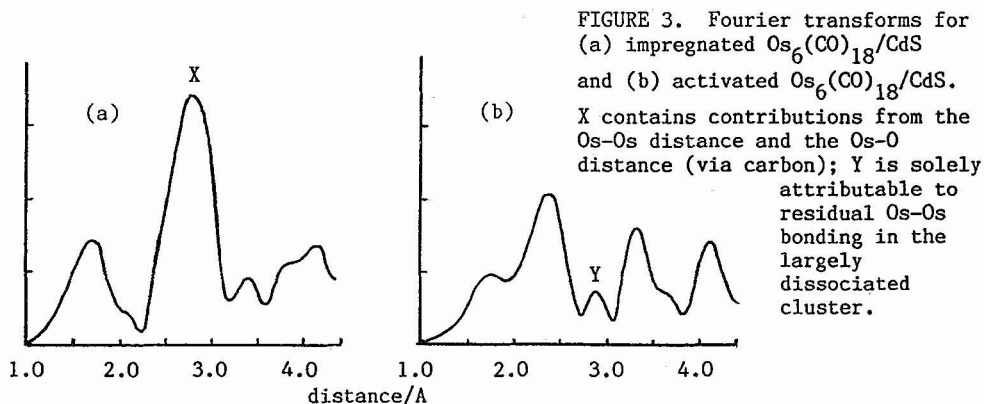


FIGURE 4. (a) EXAFS spectra of pure $\text{Os}_6(\text{CO})_{18}$ (dashed curve) and of $\text{Os}_6(\text{CO})_{18}/\text{alumina}$ (full curve). (b) Fourier transform of the spectrum of impregnated $\text{Os}_6(\text{CO})_{18}/\text{alumina}$ (full curve). The feature Z denotes the extent of retention of Os-Os bonding.

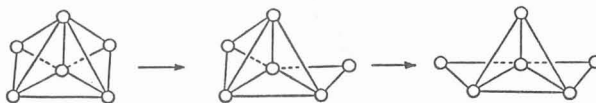


FIGURE 5. The structural unfolding that accompanies the impregnation of $\text{Os}_6(\text{CO})_{18}$ onto alumina. This structural change is inferred from the theoretical spectrum shown as the dashed curve in Figure 4b.

Conclusion. EXAFS spectroscopy is clearly and uniquely able to provide detailed information regarding the structural transformations of metal clusters at low concentrations in metal catalysts and their precursors.

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