

AN EXAFS STUDY OF THE FORMATION OF SMALL METAL AGGREGATES ON MgO USING ORGANOMETALLIC COMPOUNDS AS PRECURSORS

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Abstract:

EXAFS measurements have been carried out on very small osmium and rhenium metal particles supported on MgO. The metal particles were formed via decomposition and subsequent reduction in hydrogen of metal carbonyl clusters.

1. Introduction

Starting with molecular metal carbonyl clusters, extremely small and well defined metal particles can be prepared, allowing a detailed study of the structure of the metal particle and the metal-support interface. The surface structures resulting from decomposition of the metal carbonyl clusters are ionic complexes with metal cations bound to oxygen anions of the support. Information of the metal-cation oxygen-anion bonds in these ionic complexes can be obtained with EXAFS. [1] By a subsequent controlled reduction procedure, the formation of the metal particle and the generation of the metal-support interface can be studied in great detail with the EXAFS technique. Here we present the preliminary results of an EXAFS study of the formation of small osmium and rhenium metal particles supported on MgO using $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ and $\text{H}_3\text{Re}_3(\text{CO})_{12}$ as precursors.

2. Experimental

A stable $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ cluster was prepared by treating H_2OsCl_6 impregnated MgO (1.3 wt% Os) with a mixture of $\text{CO}/\text{H}_2 = 1/1$ at 275°C for 5 hr. [2] A subsequent reduction was carried out in flowing H_2 at 300°C for 1 hr. A $\text{H}_3\text{Re}_3(\text{CO})_{12}$ cluster was deposited on MgO (2 wt% Re) from a hexane solution under vacuum. Reduction was carried out at 500°C in flowing H_2 for 1 hr.

The treatments of the catalysts and the EXAFS experiments were performed in an EXAFS in situ cell. The samples were pressed into a thin self-supporting wafer with an optimum thickness to give $\Delta\mu x \sim 1.5 - 2.0$ at the corresponding metal LIII-edge. The EXAFS experiments were carried out at liquid nitrogen temperature with the catalysts exposed to 1 atm. H_2 . The EXAFS spectra were recorded at EXAFS station C-2 of the CHESS laboratory at Cornell (ring energy 5 GeV, ring currents 20-40 mA).

3. Data Analysis and Results

EXAFS oscillations in k space are obtained from the x-ray absorption spectrum by a cubic spline background subtraction and normalization by means of division by the height of the edge. [3] Phase shift and backscattering functions extracted from EXAFS data on Pt-foil and $\text{Na}_2\text{Pt}(\text{OH})_6$ have been used to analyze the $\text{Os}^0\text{-Os}^0$ and $\text{Os}^{n+}\text{-O}^{2-}$ EXAFS contributions. The suitability of using these platinum standards for analyzing the osmium EXAFS spectra has been discussed in [1]. Re-foil and ReO_3 have been taken as standards for the $\text{Re}^0\text{-Re}^0$ and $\text{Re}^{n+}\text{-O}^{2-}$ absorber-scatterer pair, respectively.

Fig. 1a and d present the raw EXAFS oscillations in k space of the reduced $\text{Re}(2)/\text{MgO}$ and $\text{Os}(1.3)/\text{MgO}$ samples. A k^3 forward followed by an inverse Fourier transform can isolate the first metal-metal coordination shell from higher coordination shells. The inverse Fourier transform contains also the low Z contributions present in the same r -range used for the inverse Fourier transform. Owing to the high quality of the EXAFS data and the large k range of the backscattering amplitude of osmium and rhenium the first shell metal-metal EXAFS can be reliably separated from these low Z contributions by fitting in k space starting at about $k = 7$ (\AA^{-1}). The fitting procedure results in the following first shell metal-metal coordination parameters: $N = 5.5$, $R = 2.74$ \AA , $\Delta\sigma^2 = 0.0019$ \AA^2 ($\text{Re}^0\text{-Re}^0$) and $N = 4.8$, $R = 2.62$ \AA , $\Delta\sigma^2 = 0.0027$ \AA^2 ($\text{Os}^0\text{-Os}^0$).

The presence of low Z contributions in the experimental data can now be demonstrated by using a k^1 Fourier transform which is corrected for the metal-metal phase and backscattering amplitude [4]. Fig. 1b, c, e and f show the magnitudes and imaginary parts of Fourier transforms (Os : k^1 , $\Delta k = 3.2 - 14$ \AA^{-1} ; Re : k^1 , $\Delta k = 3.5 - 13$ \AA^{-1}) of the experimental data and the EXAFS functions calculated with the metal-metal parameters given above. The differences between the solid and the dotted lines in the r range of the corresponding first shell metal-metal peak are due to the low Z scatterers present in this r range. By subtracting the calculated first shell metal-metal EXAFS function from the experimental data a difference file is obtained which contains all low Z -contributions and, if present, higher shell metal-metal contributions. To detect metal-support oxygen contributions the difference files for both samples have been Fourier transformed with a correction made for the metal-oxygen phase shift (see Fig. 2a and b).

4. Discussion

The rhenium particles created by the reduction procedure carried out in this work show a nearest neighbour coordination distance of 2.74 \AA equal to the value of rhenium bulk metal. The rhenium-rhenium coordination number of 5.5 indicates an average (spherical) particle size of about 10 \AA consisting of about 15 metal atoms. From these results one can infer that the applied reduction treatment causes the agglomeration of approximately 5 Re_3 molecular entities.

The Fourier transform (corrected for the Re-O phase shift) of the difference file (Fig. 2a) shows an interference of at least two contributions. These contributions most probably arise from scatterers present in the metal-support interface (i.e. oxygen and/or magnesium). A full analysis of the difference file will be performed in due course and published separately.

The reduction of the $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ cluster results in particles with an osmium-osmium coordination distance of 2.62 \AA which is significantly shorter than the corresponding distance in the $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ cluster (2.84 \AA). [5] This indicates that the osmium carbonyl clusters are transformed by the reduction process into osmium metal aggregates. The average $\text{Os}^0\text{-Os}^0$ coordination number ($N = 4.8$) is (within the error of ± 0.2) the same as found for the osmium carbonyl cluster, indicating the presence of spherical particles consisting of 10 atoms. Clearly, the reduction process does not lead to any sintering of the osmium metal aggregates. The Fourier transform of the difference file (Fig. 2b) shows for $1 < R < 3$ a much more complicated imaginary part as for the rhenium sample. The most probable explanation for the interference in the imaginary part is a superposition of peaks due to the same type of scatterers as present for the Re/MgO sample with peaks arising from

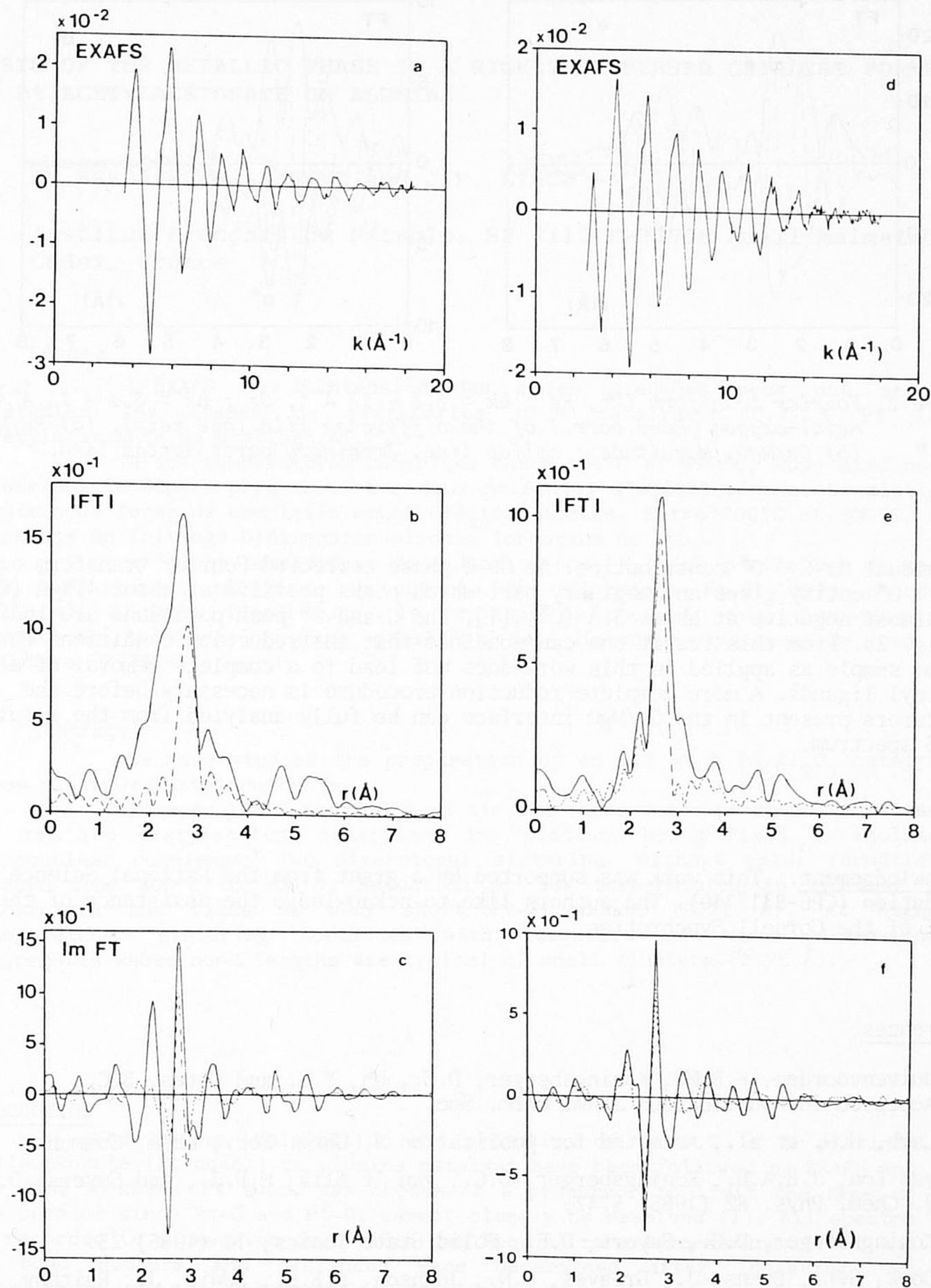


Figure 1. Data for the Re/MgO (a,b,c) and the Os/MgO (d,e,f) catalysts. Raw EXAFS spectra (a,d). Fourier transform (k^1 , Re : $\Delta k = 3.5 - 13 \text{ \AA}^{-1}$, Os : $\Delta k = 3.2 - 14 \text{ \AA}^{-1}$, metal-metal phase and amplitude corr.) of experimental data (solid lines) and calculated M^O-M^O EXAFS (dotted lines). (b,e) Magnitude. (c,f) Imaginary part.

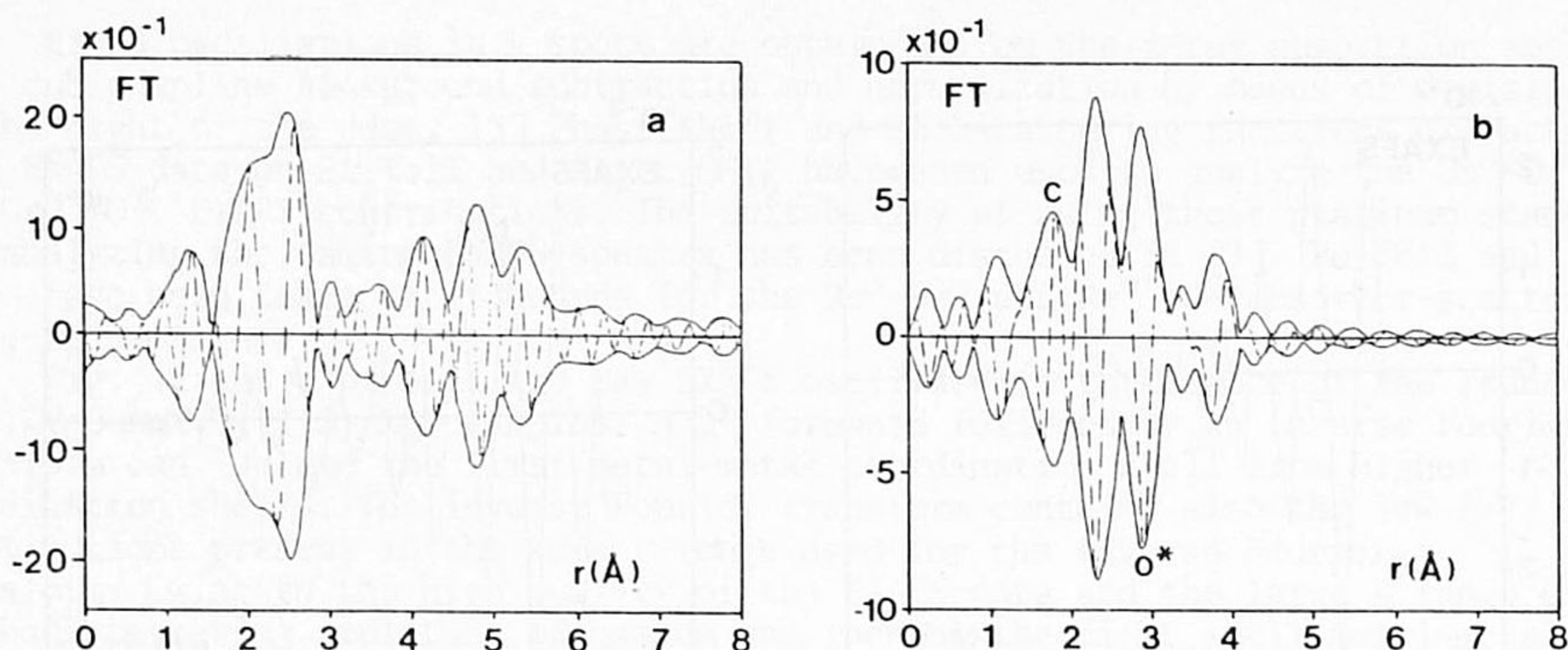


Figure 2. Fourier transform (k^1 , Re : $\Delta k = 3.5 - 13 \text{ \AA}^{-1}$, Os : $\Delta k = 3.4 - 11 \text{ \AA}^{-1}$, metal-oxygen phase corr.) of the difference file (see text). (a) Re/MgO, (b) Os/MgO. Magnitude : solide line, Imaginary part: dotted line.

a residual Os-C \equiv O* contribution. As Os-O phase corrected Fourier transform of an Os-C \equiv O* entity gives an imaginary part which peaks positive at about 1.9 Å (C) and almost negative at about 3 Å (O*) [1]. The C and O* peak positions are indicated in Fig. 2b. From this result one can conclude that the reduction conditions for the osmium sample as applied in this work does not lead to a complete removal of all carbonyl ligands. A more complete reduction procedure is necessary before the scatterers present in the Os/MgO interface can be fully analyzed from the resulting EXAFS spectrum.

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