Thermal effects on Rhodium nanoparticles supported on carbon

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Abstract. EXAFS measurements have been made in the temperature range 5 - 300 K on rhodium nano-clusters of average diameters 15.9 and 11.5 Å (rms dispersion 7.2 and 4.7 Å, respectively) supported on carbon, as well as on a Rh reference foil. The preliminary results of the first shell analysis are presented. The Debye temperature is slightly smaller in n-Rh with respect to bulk and decreases when the cluster size decreases. The results of amplitude analysis (coordination number and static DW) are sensitive to the inclusion of the 4th cumulant. In going from bulk Rh to n-Rh and decreasing the nanocluster size the average coordination number decreases and the static disorder increases. A contraction of the average nearest-neighbour distance is observed at 5 K, -0.004 Å and -0.009 Å for the larger and smaller clusters, respectively, accompanied by a very slight thermal expansion.

1. Introduction
In the last years, a big effort has been made to identify the correlation between the structure of metal nano-particles and their catalytic activity [1, 2]; the relevance not only of the ratio between surface and bulk atoms but also of the type of surface sites and of the interaction with the support has been evidenced. Standard laboratory techniques are generally insufficient to lead to a complete characterisation of nano-particles and EXAFS can give relevant complementary information on their structural and vibrational properties. Many EXAFS studies have been performed on supported and un-supported metallic clusters, but no definitive general assessments can still be made, in view of the large variability of production methods, sizes and size distributions, shapes, as well as interactions with the support and with the environment [3].

The lack of definitive conclusions make sensible to perform EXAFS measurements on a relatively new class of systems, rhodium clusters, which are actually employed for hydrogenation reactions [4, 5]. EXAFS measurements have been performed as a function of temperature (5 to 300 K) on two n-Rh samples supported on carbon, with different average diameters, determined by HAADF-STEM: 14.9 Å (rms dispersion 7.2 Å) and 10.7 Å (rms dispersion 4.7 Å), hereafter samples Rh48 and Rh72, respectively. A 12 µm reference metal foil (b-Rh) was measured too. The preliminary results of the first-shell analysis are here presented.

2. Experiment and data analysis
The n-Rh samples have been prepared following the deposition-precipitation method on activated carbon from wood with 5 weight % Rh loading and characterized by laboratory techniques such
as HAADF-STEM and chemisorption. EXAFS measurements at the Rh K edge have been performed in standard transmission configuration at the BM23 beamline of ESRF. Electron energy and average current were 6 GeV and 190 mA, respectively. The X-ray beam was monochromatized by two silicon crystals with flat (311) parallel reflecting faces; the harmonics influence was reduced by reflection from two Pt-coated mirrors. The photon fluxes were measured by ionization chambers filled with krypton gas. A Pd-Rh alloy foil maintained at room temperature and placed among the second and the third ionisation chambers gave the reference for the edge position. The samples were measured in vacuum. The temperature was varied from 5 to 300 K in a liquid helium cryostat. Three spectra were measured at each temperature. No significant edge shift was detected between b-Rh and n-Rh samples, suggesting that the interaction of n-Rh with the carbon support is negligible.

The EXAFS signals $\chi(k)$ were extracted according to a well established procedure [6]. The Fourier Transform moduli for b-Rh and for Rh72 at 5 and 300 K are shown in Fig. 1, left. The first-shell quantitative analysis has been performed by the ratio method [7, 8], taking the 5 K average spectrum of b-Rh as reference for the separate analysis of phases and amplitudes. The right panels of Fig. 1 show the phase differences $(\Phi_s - \Phi_m)/k$ and and the logarithms of amplitude ratios $\ln(A_s/A_m)$ for all the spectra ($s$) of Rh48 and Rh72 measured at 5 K compared with b-Rh ($m$) at the same temperature. Phase differences are fitted by a straight line whose intercept and slope give the difference of the first and third cumulants, respectively, of the effective distance $d$ distributions of nano-clusters with respect to bulk. Logarithms of amplitude ratios are best-fitted by a polynomial in $k^2$, whose intercept is $\ln(N_s/N_m)$ and the linear and quadratic terms give the difference of the second and fourth cumulants, respectively, of nano-clusters with respect to bulk. The results from the ratio method have been confirmed by non-linear best fit of theoretical spectra generated by the FEFF6 code [9, 10].

3. First-shell results

3.1. Thermal and static disorder, coordination number
To quantify the effects of thermal disorder, a Debye correlated model has been fitted to the temperature dependence of the second cumulant of the three samples. For b-Rh, a Debye temperature $\theta^b_D=359.3\pm0.7$ was found. The results for nanoclusters are summarised in Table 1. The Debye temperature decreases in going from b-Rh to Rh48 to Rh72.

The comparison between n-Rh samples and b-Rh allowed us to evaluate the ratio of coordination numbers and the static contribution to the width of the distribution of distances, $\sigma^2_{st}$ (Table 1). The average coordination number decreases when going from b-Rh to Rh48 to Rh72. The contribution of static disorder is larger for Rh72 than for Rh48 (the structural disorder
Table 1. First-shell Debye temperatures, coordination numbers, static disorder and bond-length contraction at 5 K. The apices “n” and “b” stay for nano, and bulk, respectively.

|          | Without 4th cumulant | With 4th cumulant |
|----------|----------------------|-------------------|
|          | $\theta_n^b/\theta_D$ | $N_n^b/N^b$ | $\sigma_{stats}^2$ (Å²) | $\Delta C^*_1$ (Å) | $N_n^b/N^b$ | $\sigma_{stats}^2$ (Å²) | $\Delta C^*_1$ (Å) |
| bulk     | 1                    | 1                | 0                        | 0                         | 1            | 0                        | 0                         |
| Rh48     | 0.959 ±0.013         | 0.691            | 0.00172                  | -0.0046                   | 0.735        | 0.00241                  | -0.0039                   |
| Rh72     | 0.955 ±0.008         | 0.649            | 0.00207                  | -0.0104                   | 0.707        | 0.00302                  | -0.0095                   |

Figure 2. Second cumulant of the first coordination shell. The static contribution is determined by comparing the amplitudes of the EXAFS signals of nano-Rh and bulk Rh taking into account only the difference of the second cumulant (a) or also the difference of the 4th cumulant (b).

In bulk Rh was considered negligible. Both coordination numbers and static contributions to disordered have been found independent of temperature. The absolute values of the second cumulants of the three samples (static plus thermal disorder) are shown in Fig. 2.

It is noteworthy that the inclusion, in the amplitude analysis, of the fourth cumulant, which measures the symmetric deviations of the distribution of distances from a normal shape (Fig. 1, right) gives rise to significantly higher coordination numbers and static disorder contributions (Table 1 and Fig. 2) with respect to a standard analysis including only the second cumulant.

3.2. Nearest neighbour distance and thermal expansion

The relation between the first cumulant $C_1$ of the effective distribution, directly determined by the ratio method, and the first cumulant $C_1^*$ of the real distribution depends on the width of the distribution, measured by the second cumulant, as well as on the photo-electron mean free path. As previously observed, different values of the second cumulant were obtained depending on the exclusion or inclusion of the fourth cumulant in the data analysis. As a consequence, the differences between the average distance in n-Rh samples and in b-Rh are different for the two procedures of data analysis, including or not the fourth cumulant (Table 1 and Fig. 3).

The comparison of the average nearest-neighbour distances $\langle r \rangle = C_1^*$ of the three samples is made in Fig. 3, where the nearest-neighbour distance in bulk Rh at 5 K has been taken as reference. For b-Rh, no static disorder is assumed and the average $\langle r \rangle$ is assumed to be only over the thermal configurations. For the n-Rh samples, the average is over the convolution of both thermal and structural configurations. There is an evident contraction of the average nearest-neighbour distance in going from bulk to Rh48 to Rh72. The thermal expansion is slightly weaker for n-Rh than for bulk Rh.
4. Conclusions
The absence of edge shift suggests that n-Rh clusters have negligible interaction with the carbon support. The Debye temperature has been found slightly smaller in n-Rh with respect to b-Rh and decreasing when the cluster size decreases. The results of amplitude analysis (coordination number and static DW) are non-negligibly sensitive to the inclusion of the 4th cumulant. In going from b-Rh to n-Rh and decreasing the nanocluster size, the average coordination number decreases and the static disorder increases. A contraction of the average NN distance is observed at 5K, -0.004 Å (Rh48) and -0.009 Å (Rh72), accompanied by a very slight thermal expansion.

Further work is in progress a) to extend the data analysis to the outer shells, b) to take into account the effects of the dependence of the photoelectron mean free path on the cluster size, c) to check the reliability of the cumulant approach to account for structural disorder in nano-particles, and, in case, to understand the physical meaning of the fourth cumulant.

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Figure 3. Average nearest-neighbours distances in bulk Rh (diamonds), in Rh48 (circles) and Rh72 (squares) relative to the distance in bulk Rh at 5 K. The real distances were calculated from the effective distances (as obtained by the ratio method) assuming a mean free path $\lambda = 9$ Å and a distribution width evaluated taking into account only the second cumulant (a) or also the 4th cumulant (b).