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Local structure and lattice dynamics of supported Rh nano-clusters for catalysis: PDF and EXAFS combined study

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Introduction

Main aim of the proposal is a very accurate EXAFS study of the structure and lattice dynamics of Rh clusters, taking advantage of recent advances in the study of thermal effects on EXAFS of bulk systems. [1]

Metal nano-particles are widely employed in industrial reactors. Activity and selectivity of such catalyst strongly depends on the particle shape and size distribution.[2] Standard laboratory techniques such as XRPD, TEM and chemisorption are often insufficient to lead to a complete characterisation of nano-particles.[3]

EXAFS can give essential complementary information to clarify the relationship between structure and functionality of supported metal catalysts, as well as, on more general grounds, the structural and vibrational properties of metallic nano-clusters. In particular the combined analysis of the first and higher shells analysis has shown to be very informative. The interpretation of EXAFS spectra of clusters is, however, complicated by several factors, such as the distribution of cluster sizes and the difference between bulk and surface atoms in terms of inter-atomic distances and thermal properties. The connection of the few average parameters obtained from EXAFS standard analyses (coordination numbers, distances and Debye Waller factors) to the real inhomogeneous structure of clusters is a problem of paramount importance.

Temperature and size dependent EXAFS measurements can substantially contribute to solve this problem. The pioneering paper by Balerna and Mobilio [4] on Au clusters has evidenced the surface effects on the average inter-atomic distances and Debye-Waller factors (parallel MSRD). Further advances can be made by exploiting the recent results obtained on bulk crystals: detection of the difference between bond and lattice thermal expansions, evaluation of the perpendicular MSRD, disentanglement of static and thermal contributions to both parallel and perpendicular MSRDs, measurement of the third cumulant and evaluation of the thermal and static contribution to the distance distribution asymmetry.

The present proposal concerns temperature-dependent EXAFS measurements on Rh clusters supported on amorphous carbon, with size distributions centred on at least two different average diameters (1.5 and 1.8 nm), as well as on a reference Rh foil.

Experiment

EXAFS measurements have been performed at the Rh K edge (23.219 keV) using a Si(311) monochromator on four samples:

a) A Rh foil of 12 micrometer thickness

b) Three samples composed by Rh nanoparticles embedded in a C matrix (Rh 5% in weight) with different surface dispersions

a1) 48 %
a2) 58 %
a3) 72 %

All samples have been measured at 5K.

The metal foil and the samples 48% and 72% have been measured as a function of temperature from 5 K to 300 K at steps of 50 K. At least three spectra have been measured at each temperature.

Results

The visual quality of the EXAFS spectra is quite satisfactory for all samples up to the wavevector value k=17 $Å^{-1}$.

A first analysis of the nearest-neighbours contribution has been performed by the ratio method. Further refinements are under way, as well as a complete SS and MS analysis extending up to the third shell by the FEFFIT code.

The preliminary results for the first coordination shell can be summarized as follows.

a) Amplitude analysis

- A reduction of the average first-shell coordination number is observed for the nanoclusters with respect to the metal foil, by a factor 0.7 and 0.65 for the 48% and 72% samples, respectively.
- The temperature dependence of the parallel MSRD of the metal foil is well reproduced by an Einstein correlated model with frequency 5.43 THz, as well as by a Debye correlated model with Debye temperature of 356 K (to be compared with the specific heat Debye temperature 350K).
- The temperature dependence of the parallel MSRDs of the nanoclusters is very similar to that of the metal foil; a slight reduction of the Einstein frequency is anyway observed when the cluster size decreases (5.19 and 5.12 THz for the 48% and 72% samples, respectively).
- The structural contribution to the parallel MSRD amounts to about 0.00168 and 0.002 $Å^2$ for the 48% and 72% samples, respectively, comparable with the zero-point value of the purely thermal contribution.

b) Phase analysis

Less accurate results have been obtained from the phase analysis, due to signal instabilities present in some of the low temperature spectra.

- The bond thermal expansion of the metal foil is, as expected, slightly larger than the lattice thermal expansion.
- A reduction of the average nearest-neighbour distance of 0.007-0.012 Å is observed at low temperature (5K) in the clusters with respect to the metal foil, the distance decreasing when the cluster size decreases.
- The average nearest-neighbour bond thermal expansion seems to be much weaker in the nano-clusters than in the metal foil.

References

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