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Application for beam time at ESRF – Experimental Method

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Local structure in chemically synthesized Co nano-clusters by XAFS spectroscopy
CH2779 held at BM29 February - March 2009

This experiment was aimed at probing in detail the local atomic structure in nanosized Co clusters by XAFS spectroscopy.
Physical properties of metallic nanoparticles are strongly dependent on their size and the interaction of the surface ions with capping agents also play a determinant role. Therefore, in order to understand the physical properties of nanoparticles their size, size distribution and surface interactions must be strictly controlled.
In order to synthesize small monodispersed Co clusters of different sizes two different procedures have been employed:
1) medium size clusters (Co_{AOT}) have been prepared at ISMN-CNR (Palermo, Italy) laboratory by chemical reduction of cobalt(II) salts entrapped in dry sodium bis(2-ethylhexyl) sulfosuccinate. These samples were preliminary characterized by XRD and SAXS. Synchrotron radiation XRD measurements revealed 7-8 nm Co fcc clusters. TEM, HR-TEM and magnetic characterizations are under run.
2) Very small resin-supported Co clusters (Co_{K1221} and Co_{IR120}) have been prepared as resin supported particles at the Dipartimento di Scienze Chimiche of the Padova university using a template-controlled synthesis strategy, already successfully employed for the preparation of metal catalysts [COR2004]. This synthesis methods produces fine resin-supported metal particles which have proved to be i) highly monodispersed particles, which size being mainly determined by the resin pore sizes, ii) resistant to oxidation thanks to the protective action of the resins and iii) minimally interacting with the support. Samples are superparamagnetic at room temperature and preliminary TEM measurements gave a particle size around 1-2 nm. High resolution TEM measurement are scheduled for the end of March. These samples were prepared 10 days before measurements and stored under Ar atmosphere in Schlenck tubes till the XAFS measurement time.
XAFS measurements were performed in transmission geometry as a function of temperature from 25 K to room temperature (RT). Samples were prepared and kept under inert (Ar) atmosphere till the XAFS measurement time. Sample pellets were prepared mixing the Co samples with BN powders under inert atmosphere using the ESRF chemistry laboratory dry box. Highly homogeneous mixtures were prepared using the ball mill at the GILDA beamline laboratory. Therefore we acknowledge the support of Dr Muller in using the ESRF Chemistry laboratory and the GILDA beamline staff which allowed to use the ball mill.
XAFS spectra of metallic Co foil were measured in the same condition to be used as reference.
The resin supported metal clusters are often used in catalysis as the resin support provides an efficient protection against particle oxidation. In order to prove the effective oxidation stability of small resin supported clusters we measured the XANES spectra of Co_{K1221} sample after a) ageing 12 hours in air and b) 4 hours in air at high temperature (80 C) and c) 12 hours in air. The XANES only show weak changes demonstrating the effective protection of the resin support (figure 3).
Preliminary XAFS analysis on medium size samples demonstrated the negative thermal expansion effect, typical of small nanoparticles and already observed in Gold clusters [COM2008]. The accurate XAFS data analysis is now in progress.

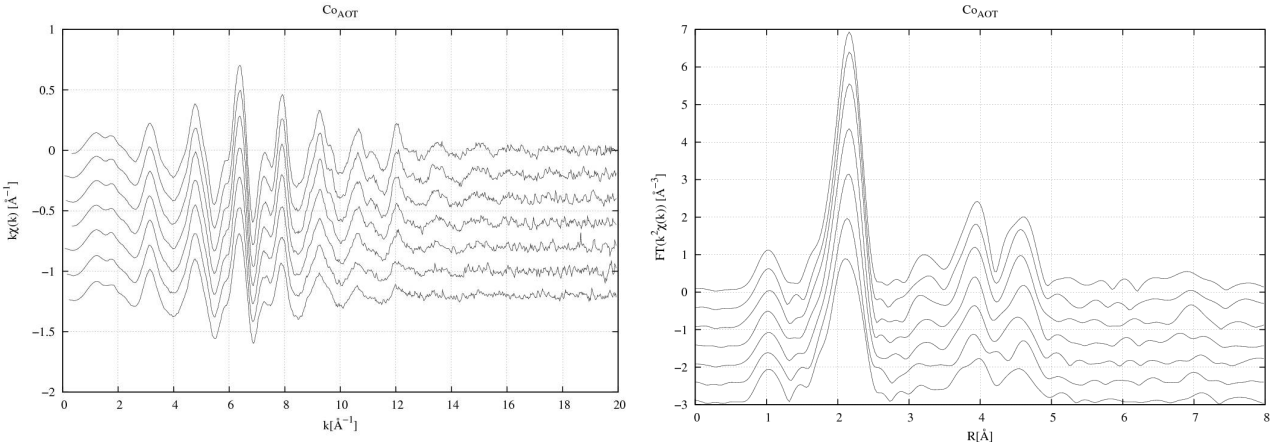

Figure 1: Co_{AOT} EXFS data as a function of temperature: kχ(k) (left and their FT (right).

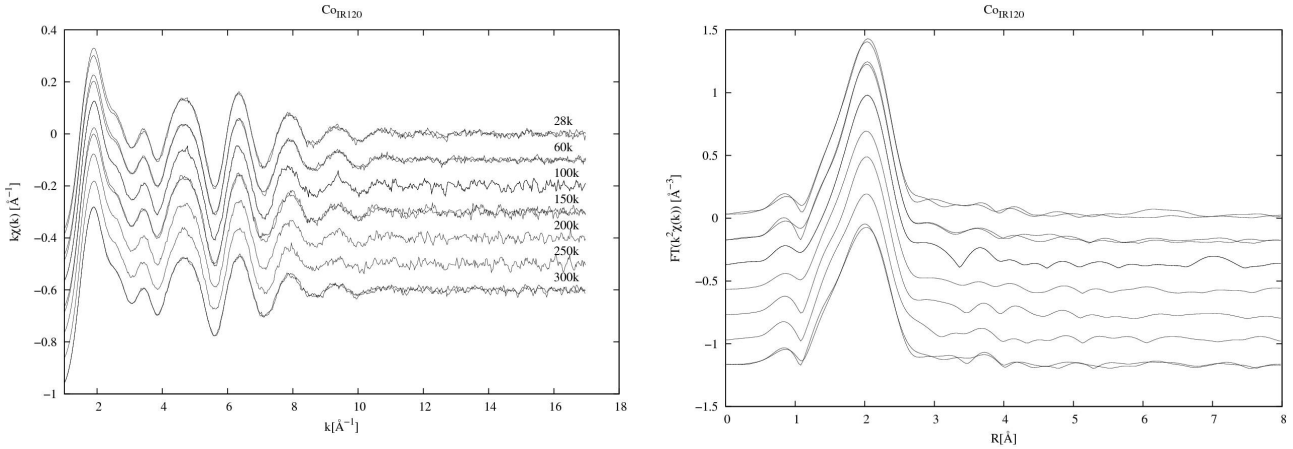

Figure 2: Co_{IR120} EXFS data as a function of temperature: kχ(k) (left) and their FT (right).

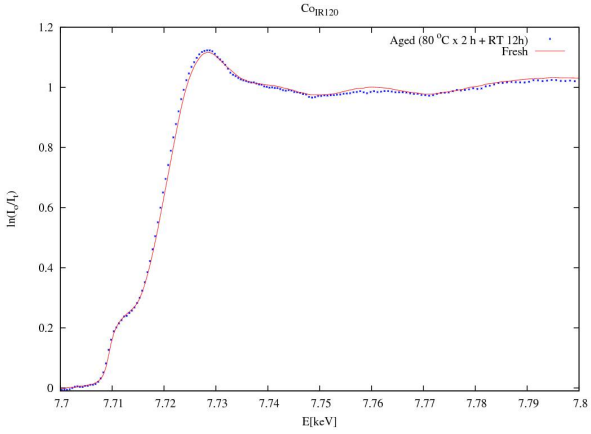

Figure 3: Co K-edge XANES spectra of fresh (red line) and aged (blue dots) Co_{IR120} sample. Ageing on air and temperature of resin supported small particles demonstrated a long therm resistance to oxidation. The small size and oxidation stability of resin supported samples makes these nanoparticles suitable for deeper investigation, for example to probe the high pressure properties of Co nanoparticles.

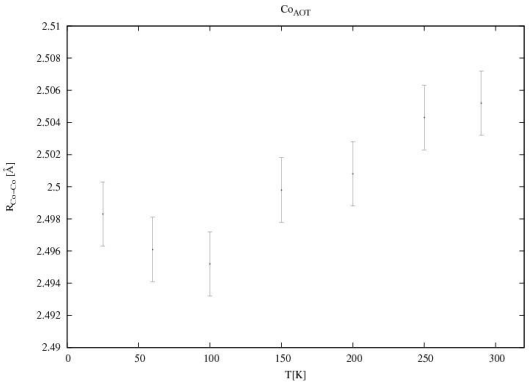

Figure 4: Preliminary XAFS data analysis on Co_{AOT} sample demonstrate a negative thermal expansion effect on Co-Co bond length.

[COR2004] B.Corain, K. Jerabek, P. Centomo, P. Canton Angew. Chem., **43**, 959-962 (2004)
[COM2008] T. Comaschi, A. Balerna, S. Mobilio, Phys. Rev. B **77** 075432 (2008).