Electronic supplementary material

Out-of-equilibrium Pt-Co core-shell supported nanoparticles stabilized by kinetic trapping at room temperature

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Extended X-ray Absorption Fine Structure Methodology

Our methodology to analyse the XAS data followed the typical procedure used in EXAFS many papers, as in ref. [1]. The XAS spectra at the Co K (7709 eV) and Pt L₃-edges (11564 eV) of supported CoPt particles and Co₃Pt bulk material were recorded at the European Synchrotron Radiation Facility ESRF (BM30 FAME station, Grenoble, France). Data were collected at 4K and at RT over an extended energy range: 11450 to 12200 keV for Pt, and 7600 to 8500 eV for Co, using a 30-element fluorescence detector. Co and Pt foils were used as references. In order to obtain the local environment around the Pt and Co atoms, simulation and fitting of the EXAFS experimental data were performed with IFEFFIT [2,3]. The k-weighted x-ray absorption fine structure function were Fourier transformed using Kaiser-Bessel window and subsequently fitted in R space (radial interatomic distance). Theoretical paths were calculated with the FEFF code using muffin tin potentials and the Hedin-Lunqvist approximation for the energy-dependent part [4]. Figure S1 shows Fourier-transformed EXAFS modulus (a) at the Co K edge and (b) at the Pt L₃ edge. From this procedure, analysis have been carried out simultaneously for the data collected at the two edges (multi-edge analysis). Such procedure allows an accurate determination of the first-shell Co-Co, Co-Pt and Pt-Pt coordination numbers N (scattered atom number), atomic distances R and mean-square deviation in R, σ². To avoid misinterpretation, many constraints have been applied: Rₚt-Co (Pt-edge)= Rₚt-Co (Co-edge) and σ²ₚt-Co = σ²ₚt-Co, and Ntot value (i.e. the average coordination number) chosen in a range in accordance with the particle size distribution deduced from TEM or GISAXS [5,6,7]. In addition, the number of neighbours was checked quantitatively to be consistent with the core size, the shell thickness, the size of choose model for each element type (Co and Pt). The compositional distribution (typically of 5%, deduced from STEM-EDX measurements on our samples prepared by UHV deposition due a low atoms mobility at RT and a high density of particles on the substrate) is enough narrow to agree to only one nanoparticle model in each
In addition, at each analysis, Co-O contributions have also been tested and appeared negligible.

Anomalous X-ray scattering Methodology

The detailed experimental procedure for data collection and data handling is described in ref. [8,9]. The small angle scattering was measured for at six energies just below the Co K and the Pt L3 edges, corresponding to a scattering factor variation of 3.4 and 6.6 electrons respectively. The analysis methods were within two types, referred as "direct method" and "differential method" [9,10]

The GISAXS intensity of the assembly of supported particles can be expressed in the local monodisperse approximation with a form factor of nanoparticles (depending on the particle
shape function) calculated in the DWBA framework. NPs morphological parameters (radius R, height H and inter-particle distance) have been extracted from GISAXS experimental data by comparison with simulations using IsGISAXS software [11]. The best results are obtained with a spherical shape that can be truncated by the substrate surface by taking an aspect ratio H/2R < 1. A narrow Gaussian size distribution with relative geometrical standard deviation close to σ(R) / R = 0.2 according to preliminarily TEM observations is used for each simulation [typically as in ref. 12]. Based on the qualitative results of the differential method, several form factors were used: homogeneous truncated sphere for alloyed and pure particles and core-shell truncated sphere for sequentially deposited particles.

- In the direct method, the intensities I(q,E) measured at different energies were fitted directly with calculated models taking into account the variation of the scattering factor with energy, extracting the morphological parameters. For example, Figure S2a shows the weak variation in the simulated profiles in the case of alloyed particles and core-shell particles of a same size. Only the Yoneda peak (the strong enhancement of the intensity originates from the interference of incoming and reflected beam) is significantly different, which is the signature of the nature of the particle external surface (Co for core Pt-shell Co and Pt-Co mixed for alloyed).

- In the differential method, the partial structure factors were first extracted by difference between the intensities measured at different energies with various levels of approximation [9]. At this stage a qualitative interpretation of the data is possible, prior to model fitting. For example, Figure S2b shows the high difference of the GISAXS profile for Pt@Co core-shell and Pt core alone particles of the same core-size distribution. In this case at the Pt-edge of the core, the intensity coming from the Pt core alone reflects the lower size effect with respect to size of the entire particle (Co shell and Pt core). In addition, the AGISAXS data analysed at both edges, enriches the quality of the interpretation, with the combination of the two methods.

Figure S2 : Example of Pt-edge GISAXS simulated (solid line) q_z out-of-plane cross-sections of (a) PtCo alloyed and Pt@Co core-shell particles of same size distribution and (b) Pt@Co
core-shell and Pt core alone particles of same core-size distribution. The measured (symbols) profile is given for comparison. This case corresponds to a typical experimental sample obtained sequentially, Pt then Co, and the final combined analysis gives \( R=1.4\text{nm}, \ H=2.3\text{nm} \) for the entire particle and \( \Delta R=0.35\text{nm} \) for the Co shell thickness. These results agree perfectly with a model of a Pt supported particle covered by a shell of two Co monolayers excepted at the substrate-Pt core interface.

**Rutherford Backscattering method**

Rutherford backscattering spectroscopy (RBS) was performed using \( \alpha \) particles of 2 MeV extracted from a Pelletron accelerator in the CEMHTI laboratory (Orléans, France). The scattering geometry is : scattering angle = 165°, exit angle 15°, incident angle 0°. The detector size is 25 mm2 and sample to detector distance is 90 mm. Typical RBS spectra of Pt-Co nanoparticles deposited on a-C/SiO2/Si(100) are shown in Fig. S3. The left side of the spectrum, at low backscattering energies, corresponds to Si and O atoms, The area under the Pt and Co peak in the high energy side of the spectrum is directly related to the number of platinum atoms in the porous substrate. The RBS spectra were fitted using the SIMNRA software, to estimate the number of deposited Co and Pt atoms and their concentration [14,15].

Figure S3: RBS spectra (red dots) and SIMNRA simulations (grey line) for an example of sample: sequential deposition of Co on Pt clusters, named Co3Pt. The peak near 1.8 MeV corresponds to backscattering from Pt atoms while the peak close to 1.55 MeV corresponds to Co atoms. The different large steps starting near 1.5 MeV, 0.75 MeV and 0.6 KeV corresponds to backscattering from Si and O atoms in the SiO2 layer and the Si substrate. The CoPt composition and quantity of atoms were obtained by simulation of the first layers and of the substrate from SIMNRA software as shown in this figure.
References: