TEM/STEM characterizations of Ni_xPt_{1-x} nano-alloys

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A wide-range of potential applications uses nanoparticles (NPs) as catalysts and requires precise control of their structure and composition. Therefore, in order to obtain NPs with well-defined structural parameters, we did a colloid chemistry synthesis. This technique is a robust method for preparing monodisperse alloyed NPs with control over size and shape and homogeneous compositions. Ni_xPt_{1-x} NPs were synthesized using platinum (II) acetylacetonate and nickel (II) acetylacetonate reduced by 1,2-hexadecandiol in organic solvent with surfactants (oleylamine and oleic acid). Generally, this method gives core-shell structures [1-3] NPs as shown on Figure 1a to 1c because of the significant difference between Ni^{2+}/Ni (-0.253 V) and Pt^{2+}/Pt (+1.18 V) reduction potentials. Nonetheless, this problem was solved by strict control of the synthesis temperature.

Reaction was modulated to obtain Ni_3Pt, NiPt and $NiPt_3$ uniformly alloyed NPs. This synthesis gave spherical or icosahedral crystalline nanoparticles with a narrow distribution size (Table 1). Conventional and HRSTEM images (CM20 - FEI, Libra 200 FE-Zeiss, Titan G2 Cs-corrected - FEI operating at 200kV) of the NPs show lattice fringes with inter-fringe measured corresponding to {111} or {200} planes of Ni-Pt alloy in a disordered face-centered cubic (FCC) structure. Lattice parameters (obtained by electron diffraction) plot as a function of the concentration of atoms in Ni_xPt_{1-x} NPs, presents a Vegard's law like bulk alloys (Figure 2). Local Energy Dispersive X-ray (EDX) measurements with STEM in chemical mapping mode, operating at 200kV, (Table1), determined Ni_xPt_{1-x} nanoparticles composition. EDX cartographies confirm a homogeneous repartition of nickel and platinum concentration into nanoparticles (Figure 1).

In order to carry out NPs behavior for high temperature catalytic applications, we have also performed *in-situ* transmission electron microscopy techniques (modified FEI - TITAN Cs-corrected ETEM), operating at 300kV, with atomic-resolution. We investigated the nanostructure - diameter and crystalline - evolution in a [25 °C - 900 °C] temperature range. The particles remain crystalline up to 800°C. When the temperature increases up to 900°C, only the core of NPs is still ordered. A statistical study was performed on the NPs size. A 1 nm fluctuation was detected on the projected diameters during temperature increase, easily lighten by drift and/or rotation of icosahedral shaped particles (Figure 3). Furthermore, from 150°C, small, close, spherical particles can coalesce.

To conclude, Ni_3Pt, NiPt, $NiPt_3$ alloyed nanoparticles with a similar diameter were synthesized by colloidal route with a very good reproducibility. An analysis of sizes, aggregation states, the chemical compositions, the lattice parameters and temperature behaviors were performed thanks to the wide range of possible techniques offered by Transmission Electron Microscopy.

References:

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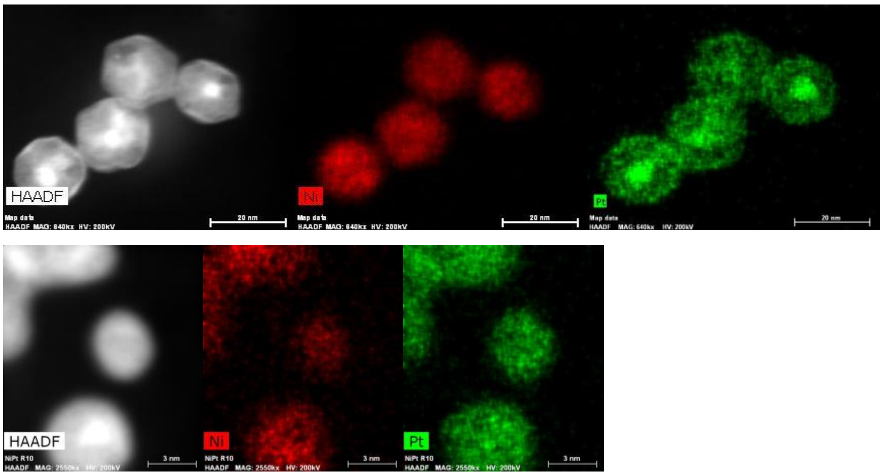


Figure 1 : *HAADF-STEM (High resolution high-angle annular dark-field imaging) NPs of (top) Ni_3Pt core-shell image where Pt presents a stronger contrast than Ni and (bottom) an uniform Ni_3Pt NPs contrast which are confirmed by local EDX - Ni (K line) and Pt (M line) chemical mapping*

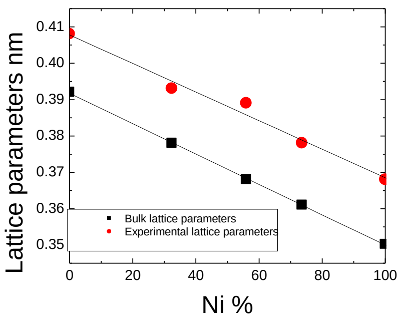
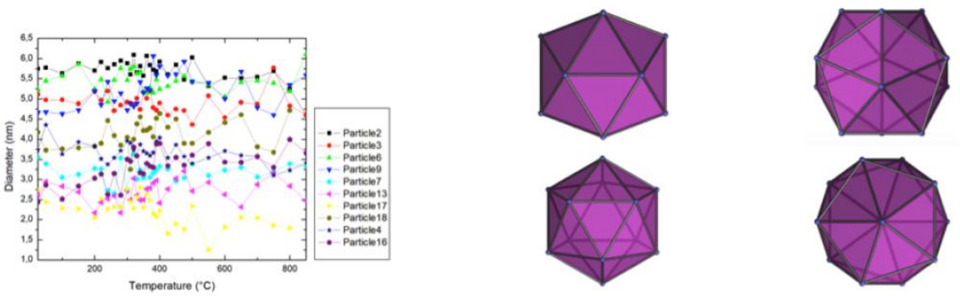


Figure 2: *Lattice parameters plot as a nickel percentage function highlight a Vegard's law as found into bulk alloys. However, one can observe a 4 % decrease of the NPs lattice parameters unambiguous associate with surface effects.*



(a) (b)

Figure 3: (a) 19 NPs diameter variations during temperature rise. The 1 nm fluctuation detected can be explained by the different icosahedral projections as shown on (b).