

Unexpected, spontaneous and selective formation of colloidal Pt₃Sn nanoparticles using organometallic Pt and Sn complexes†

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The facile and selective synthesis of small crystalline Pt₃Sn alloy nanoparticles was performed at room temperature under H₂, using a colloidal approach without the use of extra-stabilizing ligands. The Pt₃Sn alloy was found to be obtained spontaneously as the unique phase regardless of the number of tin equivalents introduced.

Pt containing bimetallic particles have been extensively studied due to their applications in the field of heterogeneous catalysis. Among these systems, Pt–Sn bimetallic catalysts are of great interest for several attractive reactions such as reforming,¹ dehydrogenation of linear paraffins or alkyl aromatics, hydrogenation of chloronitrobenzene,² but also for the oxidation of CO in fuel cells technologies.³ In the last ten years, various Pt–Sn/silica or alumina supported catalysts have been reported but due to the complexity of Pt_xSn systems (different phases often coexisting), a clear understanding of the “structure–activity” relationship could not be easily obtained.⁴ Of the classical preparation methods of such Pt_xSn systems, one route consists in the tin and platinum salts impregnation followed by high temperature treatment or in the post-grafting of organometallic tin precursors (tin alkyls or tin hydride) on pre-formed Pt particles followed by high temperature treatments (> 300 °C).^{1,5} Developing methodologies leading to the selective formation of Pt_xSn phases at low temperature by a colloidal approach is still a challenge. To date, the synthesis of Pt_xSn nanoparticles (NPs) at room temperature has been reported but the bimetallic colloid exhibited deviations from a uniform Pt₃Sn alloy phase.⁶ Another example of a Pt_xSn colloid was recently investigated but the synthesis required high thermal treatment (300 °C).⁷

We describe herein a facile and selective synthesis of small crystalline Pt₃Sn NPs and their full characterization. The preparation of the NPs was performed at room temperature, by contacting

Pt and Sn complexes [Pt(dba)₂ (dba = dibenzylidene acetone) and (n-Bu)₃SnH] under H₂ without the use of stabilizing ligands.

In a typical synthesis, NPs were obtained by contacting Pt(dba)₂ (100 mg, 0.15 mmol) in THF with 1 equivalent of tributyltin hydride (43 mg, 0.15 mmol). The reaction mixture was stirred under H₂ (3 bar) during 10 h. The colloidal suspension was purified by solvent evacuation to dryness and by several washings with dry pentane (3 × 50 mL) to remove tin precursor in excess, dba and its hydrogenated forms. Elemental analysis and EDX measurements performed on the resulting colloid gave comparable Sn/Pt ratios of *ca.* 0.4 ± 0.1 (Pt = 50.8 wt% and Sn = 11.1 wt%) and 0.5 ± 0.2 respectively. Note that EDX measurements were performed both on several different single particles (ranging from 2 to 4 nm) and on broader areas containing several particles and that the experimental Sn/Pt ratio of *ca.* 0.5 was obtained in all cases (see Table S1†). The value of 0.5 for the Sn/Pt ratio given by elemental analysis and EDX is discussed below (after Mössbauer results).

The existence of Sn-alkyls fragments at the surface of the nanoparticles was investigated by IR spectroscopy: The spectrum of the NPs exhibited the characteristic vibration bands of alkyl groups (ν_{asym} and ν_{sym} (CH₃) and (CH₂) were respectively observed at 2960 ± 10 cm⁻¹, 2870 ± 10 cm⁻¹, and 2925 ± 10 cm⁻¹, 2855 ± 10 cm⁻¹). In comparison to the free Sn precursor, the absence of the ν (Sn–H) band at 1805 cm⁻¹ indicated the loss of hydride during the reaction (Fig. 1).

It is worth noting that blank reactions performed without addition of the Pt complex did not lead to the reduction of the

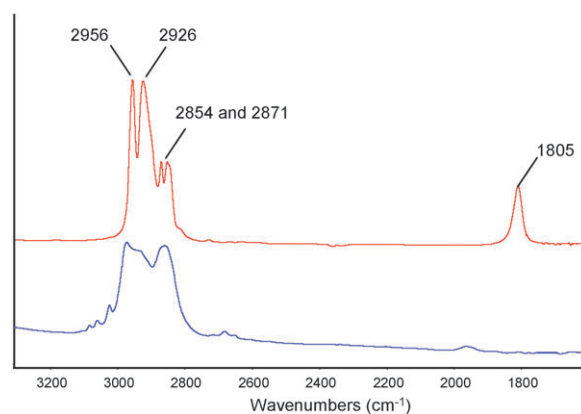


Fig. 1 IR spectra of the free HSn(C₄H₉)₃ ligand (above, red line) and of the Pt₃Sn nanoparticles prepared using 1.0 equivalent of tin precursor (below, blue line).

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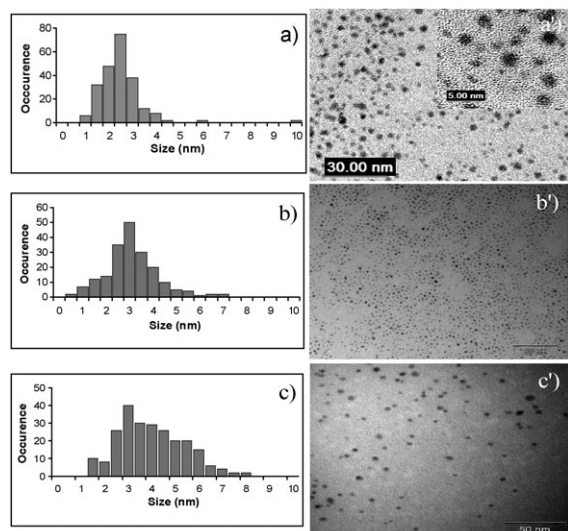


Fig. 2 Size histogram of Pt-Sn nanoparticles (a: 1 equiv. of Sn, b: 0.5 equiv. of Sn, c: 0.3 equiv. of Sn is used) and corresponding TEM micrographs of the nanoparticles solutions (bar scales: a' = 30 nm and 5 nm, b' = 50 nm and c' = 50 nm).

tin precursor into Sn⁰ particles (no particles detected by TEM, $\nu(\text{Sn-H})$ band still present in the IR spectrum, See Fig. S1–S2†).

The TEM micrographs of the NPs solution (see Fig. 2) showed the presence of isolated spherical nanoparticles with a narrow size distribution centred at 2.4 nm when 1 equiv. of Sn was used (size distribution histogram of *ca.* 200 particles in Fig. 2). When lowering the initial Sn/Pt ratio, size distributions were broader and centered at 3 nm and 4–5 nm respectively when 0.5 equiv. and 0.3 equiv. of tin were used.

The NPs mean size given by TEM was in accordance with the crystallite size estimation by wide-angle X-ray diffraction (using the Scherrer model): 4 ± 0.5 nm (for 0.3 equiv. of Sn), 3 ± 0.5 nm (for 0.5 equiv. of Sn) and < 2.5 nm (for 1 equiv. of Sn) (Fig. 3). This latter technique confirmed that the NPs obtained with our methodology are crystallized but the composition of these nanoparticles could not be established (due to the important broadness of the peaks).

The chemical nature of the crystallized core of the NPs was thus investigated by high resolution electron microscopy and the micrographs exhibited the crystallographic arrangements of Pt-Sn lattice fringes (see Fig. 2a,b and see SI-Table S2 for lattice fringes values†). Several particles (ranging from 2 nm to 4 nm,

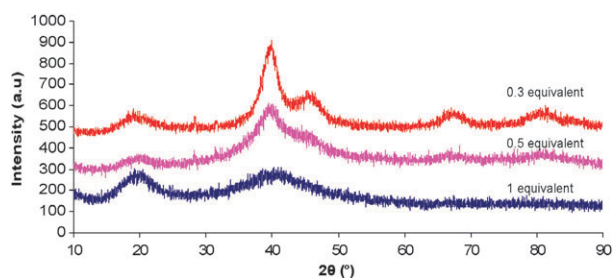


Fig. 3 Wide-angle X-ray diffraction pattern of the Pt₃Sn NPs prepared using respectively 1.0, 0.5 and 0.3 equivalent of tin precursor.

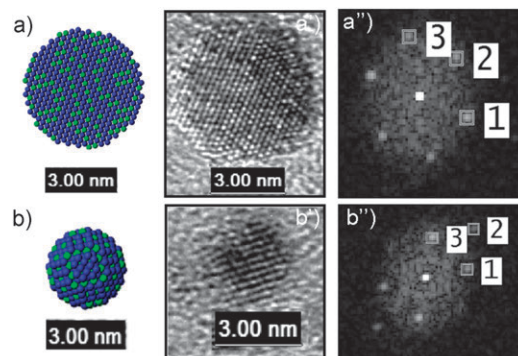


Fig. 4 (a,b) Modelling of two Pt₃Sn particles, (a',b') TEM micrographs, and (a'',b'') TEM diffraction micrographs (a,a'',a'' for the 4 nm sized particle and b,b',b'' for the 2.4 nm sized particle). The numbers 1,2,3 refer to the three vectors used for crystallographic indexing (Miller indexes of the reticular plans and angles) in Table S2.†

Fig. 2a'',b'') were studied by TEM diffraction and their diffraction patterns were compared to those of theoretical Pt⁰ and Pt_xSn phases ($x = 3$ and 1, JCPDS no. 65-0958 and no. 89-2056): the experimental Miller indexes (h,k,l) and the different angles fully fitted with those of the Pt₃Sn alloy phase and not to any other phase, in particular Pt-Sn alloy (Fig. 4 and SI-Table S2†). The alloy NPs were further investigated by Mössbauer spectroscopy (Fig. 5). For the two samples using 0.3 and 1 equiv. of tin, the observed isomeric shifts (respectively 1.44 mm s^{-1} and 1.72 mm s^{-1}) were clearly consistent with the published values for Pt₃Sn⁸ and confirmed the sole formation of Pt₃Sn alloy whatever the initial tin amount.

These results are in sharp contrast with what was previously observed for the stabilization of NPs with organosilane ligands:⁹ (i) the initial amount of organosilane has no influence on the NPs size distribution (if at least 0.2–0.3 equiv. of Si is used), (ii) the NPs are monometallic (Pt⁰) and capped by Si(alkyl) groups *via* surface Pt-Si bonds (no incorporation of Si atoms in the particles core). In the present case, the initial amount of tin precursor is important and at least 0.5 to 1 equivalent is needed to generate small nanoparticles. These nanoparticles exhibit a Sn/Pt ratio of *ca.* 0.5 (elemental analysis and EDX) which can be

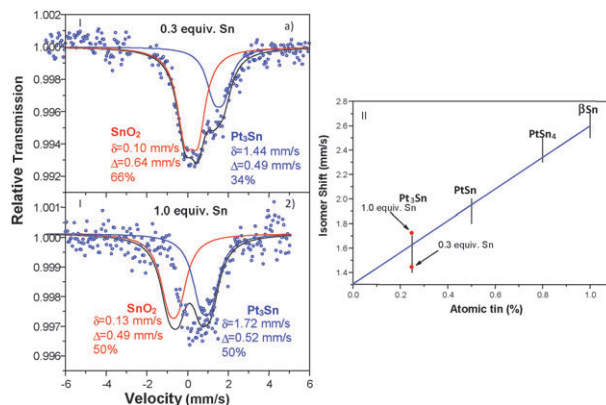


Fig. 5 (I) Mössbauer spectrum of the Pt₃Sn nanoparticles prepared using respectively (a) 0.3 and (b) 1.0 equiv. of tin precursor, (II) IS-Sn% correlation diagram (this diagram has been drawn from experimental data previously published).⁸

explained as follows: *ca.* 0.3 equivalent of tin is incorporated in the crystalline alloy core of the particles (nominal Sn/Pt ratio for Pt₃Sn phase is 0.33) and *ca.* 0.2–0.3 equivalent of Sn is present as a layer of Sn(alkyl) fragments at the surface of the particle and limits the size expansion of the particles to *ca.* 2.5–3 nm (comparable equivalents of silane ligands are needed to limit crystalline monometallic Pt or Ru particles size expansion to *ca.* 2.5 nm with similar experimental conditions).

From these observations, an hypothetical growth mechanism of the Pt₃Sn particles and their size limitation (depending on the initial Pt/Sn ratio) could be explained (but would need deeper investigation) as follows: under H₂, Pt atoms are generated from Pt(dba)₂ with the release of dba (and its hydrogenated forms). Pt⁰ atoms can further interact with the tin precursor *via* the formation of Pt–Sn bonds and can ease the cleavage of close Sn–alkyl bonds (noteworthy, the cleavage of Sn alkyls bonds and the subsequent reduction of H–Sn(Bu)₃ are not observed under H₂ without Pt). The alloy of Pt–Sn thus spontaneously nucleates and grows until all the platinum is consumed. The excess of Sn precursor present in the reaction mixture can further interact with the surface of the NPs inhibiting the agglomeration of small size nanoparticles into bigger ones (as observed when the excess of tin precursor is lower).

From this study, several conclusions can be drawn: (i) regardless of the amount of tin precursor introduced at the beginning of the NPs synthesis, only Pt₃Sn alloy is formed at room temperature. (ii) An excess of tin precursor (> 0.5 equiv. of Sn/Pt) is necessary to stabilize the particles and to limit their size expansion to very small mean size.

In summary, a simple and reproducible methodology for the preparation of small (*ca.* 2.4 nm) crystalline Pt₃Sn alloy particles afforded the spontaneous and selective formation of Pt₃Sn alloy. The Sn/Pt initial ratio was found to govern the mean size of the NPs and the broadness of size distribution but not the alloy phase! These observations suggest that spontaneous formation of Pt₃Sn alloy is driven by thermodynamic

considerations and that the size limitation of the NPs is due to the stabilizing properties of the surface organometallic tin compound.

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Notes and references

- (a) G. Meitzner, G. H. Via, F. W. Lytle, S. C. Fung and J. H. Sinfelt, *J. Phys. Chem.*, 1988, **92**, 2925–2932; (b) R. D. Cortright, J. M. Hill and J. A. Dumesic, *Catal. Today*, 2000, **55**, 213–223; (c) G. J. Siri, J. M. Ramallo-Lopez, M. L. Casella, J. L. G. Fierro, F. G. Requejo and O. A. Ferretti, *Appl. Catal., A*, 2005, **278**, 239–249; (d) F. Humblot, J. P. Candy, F. Le Peltier, B. Didillon and J.-M. Basset, *J. Catal.*, 1998, **179**, 459–468.
- B. Coq, A. Tijani and F. Figueras, *J. Mol. Catal.*, 1992, **71**, 317–333.
- (a) M. M. Schubert, M. J. Kahlich, G. Feldmeyer, M. Huttner, S. Hackenberg, H. A. Gasteiger and R. Behm, *Phys. Chem. Chem. Phys.*, 2001, **3**, 1123–1131; (b) M. Arenz, V. Stamenkovic, B. B. Blizanac, K. J. J. Mayrhofer, N. M. Markovic and P. N. Ross, *J. Catal.*, 2005, **232**, 402–410.
- C. Dupont, Y. Jugnet and D. Loffreda, *J. Am. Chem. Soc.*, 2006, **128**, 9129–9136.
- (a) F. Humblot, D. Didillon, F. Lepeltier, J.-P. Candy, J. Corcoran, O. Clause, F. Bayard and J.-M. Basset, *J. Am. Chem. Soc.*, 1998, **120**, 137–146; (b) R. Burch, *J. Catal.*, 1981, **71**, 348–359.
- H. Bönemann, P. Britz and W. Vogel, *Langmuir*, 1998, **14**, 6654–6657.
- Z. Liu, D. Reed, G. Kwon, M. Shamsuzzoha and D. E. Nikles, *J. Phys. Chem.*, 2007, **111**, 14223–14229.
- (a) V. I. Kuznetsov, A. S. Belyie, E. N. Yurchenko, M. D. Smolikov, M. T. Protasovan, E. V. Zatolokina and V. K. Duplyakin, *J. Catal.*, 1986, **99**, 159–170; (b) R. Bacaud, P. Bussière and F. Figueras, *J. Catal.*, 1981, **69**, 399–409; (c) A. Svane and E. Antonicik, *Phys. Rev. B: Condens. Matter*, 1987, **35**(10), 4611–4624; (d) R. Srinivasan, R. Sharma, S. Su and B. H. Davis, *Catal. Today*, 1994, **21**, 83; (e) J. Olivier-Fourcade, J. Womes, J.-C. Jumas, F. Le Peltier, J. Morin and B. Didillon, *ChemPhysChem*, 2004, **5**, 1734–1744.
- (a) K. Pelzer, B. Laleu, F. Lefebvre, K. Philippot, B. Chaudret, J.-P. Candy and J. M. Basset, *Chem. Mater.*, 2004, **16**, 4937–4941; (b) M. Boualleg, J.-M. Basset, J.-P. Candy, P. Délichère, K. Pelzer, L. Veyre and C. Thieuleux, *Chem. Mater.*, 2009, **21**, 775–777.