Electronic Supplementary Information

First direct evidence by *in situ* IR of Pt-Sn alloy surface segregation monitored by CO adsorption at low temperatures.

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Sample preparation

Pt-containing mono and bimetallic supported catalysts were synthesized using a two-step methodology. Pt and Pt-Sn nanoparticles (NPs) were first prepared using a colloidal method. A mixture of a Pt complex [i.e. Pt(dba)$_2$ (dba=dibenzylidene acetone)] and octylsilane, which acted as a ligand, was used for the synthesis of Pt monometallic NPs. Pt-Sn NPs were obtained by contacting Pt(dba)$_2$ and tributyltin hydride [(n-Bu)$_3$SnH] without the addition of any other ligand[1]. The precursors were dissolved in dry tetrahydrofuran (THF) and pressurized with H_2 (3 bar) during 10 h at room temperature. The colloidal suspension was further used for the second step of the catalyst preparation. Following the evaporation of the solvent, a small volume of the suspension was added to the γ-Al_2O_3 support (BET surface area of 106 m^2/g) under continuous stirring and non-oxidative atmosphere and then dried overnight under Ar. The dry crude catalysts were subsequently calcined under flowing dry air at 320°C in order to remove most of the alkyl fragments.

Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS)

For the DRIFTS studies, a commercial High Temp/Ambient Pressure Chamber DRIFTS cell from Spectra-Tech was used modified in a similar way as that described in details elsewhere[2]. The DRIFTS assembly was fitted in a Magna 55 Nicolet spectrometer using a MCT detector. The cell dome was fitted with ZnSe windows. The samples were used in the powder form and placed into a ceramic crucible. The control/measure thermocouple was located at the centre of the sample bed. Spectra were collected using 32 scans at a resolution of 4 cm^{-1}. The DRIFTS data are reported as log 1/R, with R = I / Io, where R is the sample reflectance, Io is the intensity measured on the sample after exposure to the CO-free feed and I is the intensity measured under reaction condition. The pseudo-absorbance log 1/R gives a better linear representation of the band intensity against sample surface coverage than that given by the Kubelka-Munk function for strongly absorbing media[3]. It was shown that the IR method used here gave similar results whether transmission or DRIFTS was used[4].

Transmission electron microscopy (TEM)

Transmission electron microscopy for both the colloidal nanoparticles and solid materials were carried out at ‘Centre Technologique des Microstructures’, UCBL, Villeurbanne, France by using a High Resolution Electron microscope JEOL2100F. The acceleration voltage used was 200 kV. The samples were dispersed in THF and the carbon-coated copper grids were impregnated with a droplet of the mixtures. The mean size of the Pt and Pt-Sn nanoparticles in the colloidal state was ~ 2 nm. The narrow particle size distribution was maintained after the deposition onto the support and after calcination at 320°C.

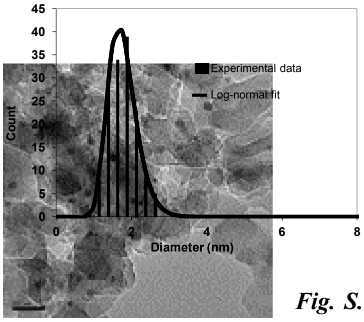

Fig. S.1. TEM picture and particle size distribution of Pt NPs supported onto γ-Al_2O_3

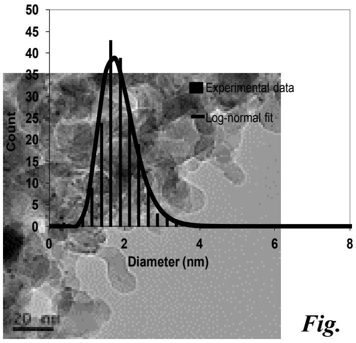

Fig. S.2. TEM picture and particle size distribution of Pt-Sn NPs supported onto γ-Al_2O_3

Inductively coupled plasma (ICP)

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[1] M. Boualleg, D. Baudouin, J-M. Basset, F. Bayard, J-P. Candy, J-C. Jumas, L. Veyre, C. Thieuleux, Chem.Commun., 2010, 46, 4722–4724.

[2] F. C. Meunier, A. Goguet, S. Shekhtman, D. Rooney, H. Daly, Appl.Catal. A: Gen., 2008, 340, 196.

[3] J. Sirita, S. Phanichphant, F.C. Meunier, Anal.Chem., 2007, 79, 3912.

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The ICP technique was used for the determination of the elemental composition of the Pt-Sn/γ-Al_2O_3 and Pt/γ-Al_2O_3 samples. After an acidic treatment of the samples, the nominal loading found were 0.86 wt. % for Pt/γ-Al_2O_3 and 0.65 % wt. Pt for Pt-Sn/γ-Al_2O_3. The tin content in the Pt-Sn based sample was 0.61 wt. %.

In situ X-ray diffraction (XRD)

The data collection was performed on the blank support γ-Al_2O_3 and on both samples, Pt-Sn/γ-Al_2O_3 and Pt/Al_2O_3 pre-reduced *in situ* under 20mL/min H_2 flow at 400°C for 1h. The samples were then cooled down to 25°C under H_2. The diffraction patterns were collected in the 2θ angle range [25°-90°]. The presence of Pt-Sn crystallites was supported by the presence of two peaks at 2θ = 41-45° and 2θ = 79°, which are consistent with a phase $Pt_{0.996}$ $Sn_{1.004}$. Pt crystallites are represented by two peaks at 2θ = 40° and 81°, respectively. Due to the anisotropy of metal crystallite size in the case of Pt/Al_2O_3, some of the rays are hardly visible.

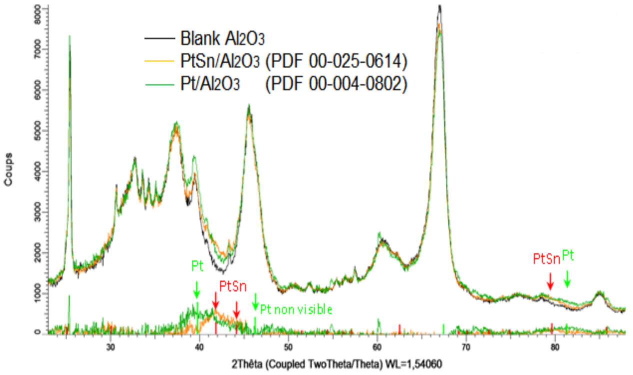

Fig. S.3. XRD patterns of plain support γ-Al_2O_3, Pt-Sn/γ-Al_2O_3 and Pt/Al_2O_3 after calcination at 320°C followed by reduction at 400°C under H_2 flow. The arrows indicate in the difference signal the presence of Pt (PDF 00-004-0802) and PtSn phases ($Pt_{0.996}$ $Sn_{1.004}$ PDF file 00-025-0614).

X-ray photoelectron microscopy (XPS)

X-ray photoelectron spectroscopy was performed on the pre-reduced Pt-Sn/Al_2O_3 at 400°C under H_2 for 1h. The apparatus used was a KRATOS Axis Ultra DLD spectrometer, equipped with a coaxial charge neutraliser and monochromated Al Kα x-ray source with a pass energy of 20 eV. The base pressure in the analysis chamber was below $5x10^{-8}$ Pa. Owing to the very low Pt concentration as well as the masking of the main Pt 4f peaks (B.E.~ 71 & 74eV) by the dominant Al 2p transition, the XPS spectra were collected for Pt 4d (Fig. S4). The B.E. value of γ-Al_2O_3, 74.0eV attributed to Al 2p has been applied as the spectral reference to calibrate all the transitions.

Table S.1. Binding energies and atomic concentration of Pt 4d, Sn 3d and Al 2p for the Pt-Sn/Al_2O_3 catalyst after reduction in H_2 at 400°C.

Element	Binding energy (eV)	Atomic conc. (%)
Pt $4d_{5/2}$	314.3	0.14
Sn $3d_{5/2}$ (a)	484.65	0.09
Sn $3d_{5/2}$ (b)	486.7	0.21
Al 2p	74	39.5

The measured Pt 4d B.E. corresponded to Pt^0. Two Sn states were visible and may be attributed to Sn^0 (peak at 484.65 eV, a value of 485.0 being reported in the literature[5]) and Sn^I or Sn^{II} (peak at 486.7, a value of 487 eV being reported elsewhere[5]). The stoichiometry of metallic species near to the surface appeared to be ca. $Pt_{1.6}Sn$. A single Al 2p peak encompassing the Pt 4f contribution was present and corresponded to Al_2O_3 (data not shown.

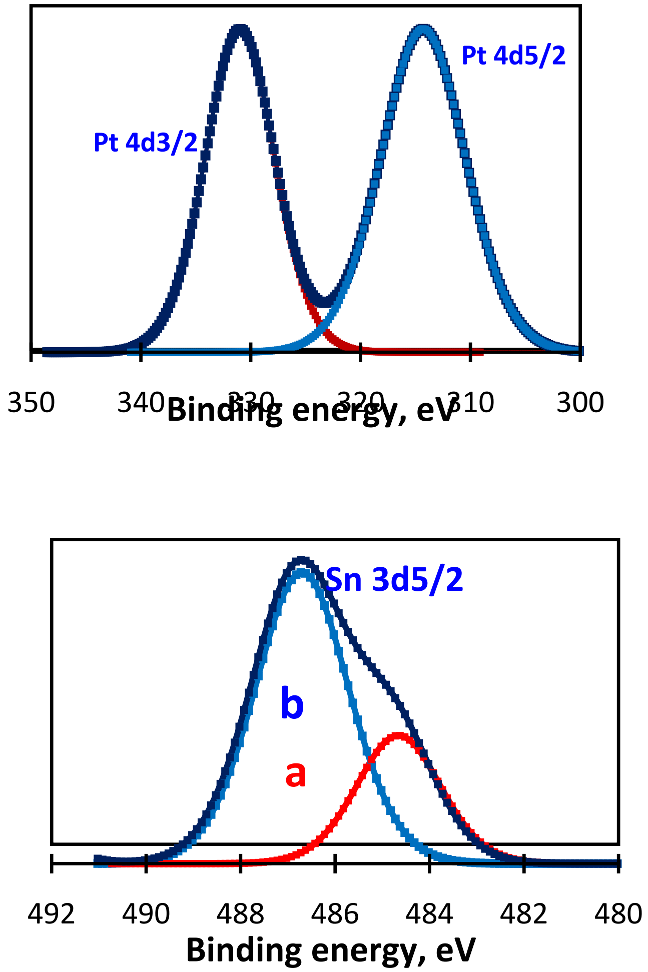

Fig. S.4. Fit of the XPS spectra collected over the Pt-Sn/γ-Al_2O_3 after calcination at 320°C followed by reduction at 400°C under H_2.

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[5] K. Balakrishnan and J. Schwank, Journal of Catalysis, 1991, 127, 287-306.