### S1. Refinement of the $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) model

The structure of the supported  $Pt_{10}Sn_3$  system was refined before investigating hydrogen adsorption, by extending the cell to 16.71 Å in the x direction, by adding new initial states before geometry optimization, and adding velocity scaled MD steps. The dimensions of the cells (before and after extension) are illustrated in Figure S1.1.



**Figure S1.1.** Top and side views of the cells for the  $Pt_{10}Sn_3$  supported cluster, (a) before and (b) after MD refinement, including an extension of the cell in the x direction.

Various strategies and morphologies were then selected to begin the optimization of a refined  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) model (Figure S1.2). The first one is the biplanar  $Pt_{13}$  cluster optimized on the support in which 3 Pt atoms replaced by Sn atoms. A geometry optimization was then performed (Figure S1.2-(a))). The second one is  $Pt_{13}$  cluster optimized in gas phase in which 3 Pt atoms are replaced by Sn and put on the support (Figure S1.2-(b)). The third one is the  $Pt_{10}Sn_3$  optimized in gas phase (by simulated annealing) and put on the support (Figure S1.2-(c)). These 3 morphologies have been then optimized on the three different alumina adsorption sites previously identified (Figure S1.2-(d)).<sup>[1]</sup> Following this first series of geometry optimizations, velocity scaled MD was used for all pre-optimized systems to reach

an even better stability of the system. These dynamics were carried out between 600 and 800 K with only the metal atoms allowed to move, while the atoms of the support remained frozen.



**Figure S1.2.** Morphologies used to begin the MD exploration for  $Pt_{10}Sn_3$  supported clusters : (a) MD optimized  $Pt_{13}$  supported cluster from reference <sup>[1]</sup>, (b) MD optimized in gas phase  $Pt_{13}$  cluster from reference [36], (c) gas phase optimized  $Pt_{10}Sn_3$  cluster, (d) preferred adsorption sites on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) from reference <sup>[1]</sup>.

# S2. Cuboctahedral $Pt_{10}Sn_3$ cluster used for the investigation of hydrogen adsorption

Hydrogen adsorption was modeled on the  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) system. The H coverage was varied between 2 to 20 hydrogen atoms per cluster, which appeared to be sufficient to saturate the cluster. The most stable  $H_0Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) system was used as a starting structure, on which hydrogen atoms were adsorbed, and the system was subjected to a velocity scaled MD study. The cluster morphology showing strong modifications at H coverage higher than 10 atoms per cluster, other investigations were made on a cuboctahedral cluster morphology (Figure S2.1) saturated by hydrogen atoms, and then with decreasing hydrogen loading. At each coverage, velocity scaled MD runs followed by quench steps were undertaken.

For all the systems containing hydrogen, a MD time step of 5 fs was used and the hydrogen atomic weight was increased to 10 g/mol. Tin acting as a hydrogen diffusion barrier, exploration of H adsorption sites on the metal cluster required the mobility of metal atoms to be taken into account also during MD, which was performed for temperatures enclosed between 800 K and 1200 K.



**Figure S2.1.** Cuboctahedral  $Pt_{10}Sn_3$  cluster morphology without H on the left, and saturated with 20H atoms on the right (before any optimization). Blue: Pt, Grey: Sn, White: H.

## S3. Structures of bulk Pt<sub>x</sub>Sn<sub>y</sub> compounds



**Figure S3.1**. Structures of platinum-tin alloys, from the Pearson database (source: MedeA software, Materials Design). Blue: Platinum; Grey: Tin. Cage and layer-like structures extracted from the periodic structures are shown below the corresponding alloys.

## S4. Bader charges for the non-supported clusters



Figure S4.1. Bader charges (mean per Sn or Pt atom) in the non-supported cluster models.

S5. Structural feature of the  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub> obtained after the simulated annealing sequence



**Figure S5.1.** Most stable morphology obtained for  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) cluster: (a) top view; (b) side view. The numbers correspond to the data given in Table S5.1. Platinum atoms are numbered in italic.

Pt-O Bond	Length (Å)	Pt-Al Bond	Length	Pt-Pt Bond	Length	Pt-Sn Bond	Length
Pt3-O	2.156	Pt3-Al	2.571	Pt3-Pt9	2.547	Sn3-Pt9	2.626
Pt6-O	2.19	Pt5-Al	2.656	Pt5-Pt8	2.569	Sn3-Pt1	2.637
Pt5-O	2.255	Pt2-Al	2.709	Pt6-Pt8	2.575	Sn1-Pt4	2.657
Pt7-O	2.261	Pt7-Al	2.809	Pt5-Pt6	2.581	Sn3-Pt7	2.664
Pt3-O	2.922	Pt6-Al	2.815	Pt2-Pt7	2.593	Sn2-Pt10	2.679
		Pt3-Al	2.948	Pt7-Pt1	2.608	Sn1-Pt1	2.681
				Pt10-Pt1	2.61	Sn2-Pt2	2.716
				Pt2-Pt6	2.638	Sn1-Pt9	2.725
				Pt4-Pt9	2.647	Sn2-Pt8	2.73
				Pt8-Pt10	2.653	Sn2-Pt6	2.751
				Pt4-Pt5	2.656	Sn1-Pt8	2.796
				Pt3-Pt7	2.706	Sn1-Pt10	2.896
				Pt4-Pt8	2.719		
				Pt3-Pt4	2.721		
				Pt4-Pt6	2.846		
				Pt2-Pt1	2.861		
				Pt6-Pt7	2.904		
Average below 2.5 Å	2.216	Average	2.751	Average	2.673	Average	2.713

**Table S5.1**. Bond lengths for the  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub> obtained after the simulated annealing sequence, reported for values below a cutoff of 3 Å.



S6. Hydrogen adsorption geometries on the  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) model

**Figure S6.1**. Most stable structures found for each investigated hydrogen coverage. Side (along x and y) and top (along z, bottom) views.

S7. Hydrogen adsorption energies on the  $Pt_{10}Sn_3/\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) model



**Figure S7.1**. Evolution of the average  $H_2$  adsorption energy on the bimetallic cluster (present work) compared to the monometallic cluster (data from ref.<sup>[2]</sup>).

#### References

- [1] C.H. Hu, C. Chizallet, C. Mager-Maury, M. Corral Valero, P. Sautet, H. Toulhoat, P. Raybaud, J. *Catal.*, **2010**, 274, 99-110.
- [2] C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet, P. Raybaud, *ChemCatChem*, **2011**, *3*, 200-207.