Supporting Information

Electronic Properties and Charge Transfer Phenomena in Pt Nanoparticles on γ-Al₂O₃: Size, Shape, Support, and Adsorbate Effects

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1. Experimental and theoretical methods

(b) Structural, electronic characterization, and nanoparticle shape modeling

- Nanoparticle shape modeling

All of our small NP (diameter < 1.5 nm) samples are characterized by narrow size distributions according to in-depth TEM analysis, while wider size distributions were observed for the larger clusters (Table I and Ref. 22). In order to determine the most representative NP shape for each of the samples, we have used volume-weighted (small NPs, S1-S6) TEM diameters. In general, the use of the volume-weighted diameters (d_{average} = \sum (d \cdot w) / \sum w, where the weighting factor w is the volume which is proportional to d³) is preferred when comparing TEM and EXAFS structural information, since EXAFS is a volume-weighted technique.

- Electronic characterization (XANES)

In our manuscript, information on the changes of the area of the Pt-L₃ absorption peak under different environmental conditions is included. Different methods have been used in the literature to calculate this area before and after NP/adsorbate exposure. Some authors first aligned all the spectra and subsequently calculated their respective difference, while others
used the area of the second feature (called peak B) observed in raw (not artificially aligned) ΔXANES spectra as the representative parameter\textsuperscript{15,16,19,20,23,24,40,41}. Such spectra were commonly obtained by subtracting NP XANES data acquired either under an inert atmosphere (He), vacuum, or at high temperature\textsuperscript{20} from those obtained under a given reactive adsorbate (e.g. H\textsubscript{2}). We have followed the second approach for the calculation of the ΔXANES areas shown within the main text of this manuscript.

2. Additional discussion

A difference between analogously-sized NPs with different shape (e.g. S1 and S2) is the strength of the peak observed at 11.58 keV (marked with a dotted vertical line), being weaker for the flatter NPs, Fig. 1. A correlation between such feature and the internal degree of crystalline order in NPs of different sizes has been discussed in the literature\textsuperscript{10,46}, and it was found to be strongly suppressed in poorly ordered NPs or in NPs of very small size.

It should be noted that in our study the WL intensity was found to only minimally change with decreasing NP size (see Suppl. Fig. 1). This is in contrast to the results of Lei et al.\textsuperscript{16} for Pt NPs with sizes ranging from 1.4 to 9 nm, but in agreement with Ankudinov et al.\textsuperscript{10}, since the latter only reported strong WL intensity variations for very small NPs (≤ 5 atoms), while our smallest NPs have about 22 atoms. Nevertheless, a small difference in the WL intensity was observed when comparing NPs of roughly the same TEM diameter (e.g. S1 and S2 or S3 and S4) but different shape (2D versus 3D). In particular, planar structures were found to show slightly higher WL intensities. This is in accord with previous theoretical predictions\textsuperscript{10}. The same group also observed nearly constant WL intensities for 3D close-packed and polytetrahedral NPs of different sizes (Pt\textsubscript{13}, Pt\textsubscript{19}, Pt\textsubscript{43}), which was assigned to a fixed Pt-5d charge count.\textsuperscript{10,18}
Suppl. Fig. 1 – Pt-L₃ XANES region [absorption coefficient, μ(E), versus E] of micellar Pt NPs on γ-Al₂O₃. The samples were measured at (a) room temperature and (b) low temperature (173 K for S1 and S2, 180 K for S8 and S9) in H₂ after reduction. Similar data from a Pt foil are also displayed for reference in (a).
**Suppl. Fig. 2:** Normalized absorption coefficient, $\mu(E)$, versus energy (XANES region) for the Pt-\(L_3\) edge of Pt NPs (~0.8 nm for S1 and S2, ~1 nm for S3 and S4) on $\gamma$-\(\text{Al}_2\text{O}_3\). Samples were measured at room temperature in $\text{H}_2$ after reduction. Similar data from a Pt foil are also shown for reference.
Suppl. Fig. 3: Shift in the energy of the Pt-L$_3$ absorption edge of Pt NPs on γ-Al$_2$O$_3$ with respect to a bulk Pt reference as a function of: (a) the 1$^{st}$ nearest neighbor (NN) coordination number (CN) and (c) the TEM NP diameter from Ref. 39 (b) Evolution of the ΔXANES area (peak B) of NPs with different sizes as a function of the 1$^{st}$ NN CN. The ΔXANES plots were obtained by subtracting XANES spectra measured in H$_2$ at 648 K (adsorbate-free) from those measured at low temperature under H$_2$ (nearly H-saturated). The minimum low temperature achieved in our experimental setup was slightly different for different samples: 173K (S1, S2), 188K (S4), 183K (S5, S6), 166 K (S7), 180 K (S8,S9).
Suppl. Fig. 4 – (a) Energy shift (LT-648 K) versus Ns/Nt. (b) ∆XANES (LT-648 K) Peak B area versus Ns/Nt, and (c) versus the number of broken bonds at the NP surface normalized by the total number of atoms within the NP (N_t) for S1-S6.
Suppl. Fig. 5: Morphology of the Pt\textsubscript{22}, Pt\textsubscript{22}H\textsubscript{25} and Pt\textsubscript{22}H\textsubscript{31} NPs obtained via DFT.