Comment on "Effect of Hydrogen Adsorption on the X-Ray Absorption Spectra of Small Pt Clusters"

In a recent Letter, Ankudinov *et al.* [1] attributed the origin of the changes observed in our experimental Pt L_2 and L_3 x-ray-absorption near-edge structure caused by H adsorption on supported Pt clusters [2] largely to a H-induced change in the local Pt potential. Since the absorption μ equals $\mu_o(1 + \chi)$, the total change, $\Delta\mu = \mu(\mathrm{H/Pt}) - \mu(\mathrm{Pt})$, can be expressed as $\Delta\mu = \Delta\mu_o + \Delta[\mu_o\chi_{\mathrm{Pt\text{-}Pt}}] + \mu_o'\chi_{\mathrm{Pt\text{-}H}}$. The three terms include changes in the existent atomic x-ray-absorption fine structure ($\Delta\mu_o$) and Pt-Pt scattering ($\Delta[\mu_o\chi_{\mathrm{Pt\text{-}Pt}}]$), and the additional Pt-H scattering ($\mu_o'\chi_{\mathrm{Pt\text{-}H}}$). Ankudinov *et al.* [1] showed with FEFF8 calculations on octahedral Pt_6 and Pt_6H_8 clusters (H in threefold sites) that the first two terms dominate in $\Delta\mu = \mu(Pt_6H_8) - \mu(Pt_6)$. We interpreted our experimental $\Delta\mu$ as resulting entirely from the last term.

We do not agree with their conclusions for two reasons: (1) both the Pt_6 and Pt_6H_8 clusters used in their calculations are not representative of our active supported Pt catalysts, and (2) the Pt-H scattering does dominate in FEFF8 results for more representative clusters. The Pt_6 cluster has a large narrow (0.2 eV) surface state falling right at the Fermi level, E_f, which is not representative of our small (*nonmetallic*) supported Pt particles, nor of other clusters as confirmed by FEFF8 calculations. Their Pt_6H_8 cluster has the H in the threefold sites; however, Kua *et al.* [3] show that H on the model Pt_6 cluster, and on most small clusters at low coverage, will preferentially adsorb in the atop positions.

Figure 1 compares FEFF8 [4] results for their Pt_6/Pt_6H_8 clusters (H in threefold hollow sites) [Fig. 1(a)] with those for our more representative Pt_6/Pt_6H_6 clusters [Fig. 1(d)]. We give the three contributions and the total difference $\Delta\mu$. Figure 1(a) is consistent with their conclusions (i.e., $\Delta[\mu_o\chi_{\mathrm{Pt\text{-}Pt}}]$ dominates and $\Delta\mu_o$ is comparable to $\mu_o'\chi_{\mathrm{Pt\text{-}H}}$). Figure 1(d) shows results when the H atoms are moved to the atop position and the "artificially" large density of states (DOS) at E_f has been removed by shifting E_f upward by 0.2 eV to better approximate the (*nonmetallic*) small Pt particles in our experiments. The $\Delta\mu_o$ and $\Delta[\mu_o\chi_{\mathrm{Pt\text{-}Pt}}]$ contributions are now drastically reduced. Figure 1 also shows intermediate results when just the H is moved to the atop positions [Fig. 1(b)] or just the Fermi level is shifted [Fig. 1(c)]. The total $\Delta\mu$ line shape in Fig. 1(d) reproduces most of our adsorbed H [2], S, and O [5] experimental results.

The Ankudinov Pt_6/Pt_6H_8 results are nearly appropriate for H adsorption on bulk Pt (threefold H adsorption and large DOS at E_f) and for large *metallic* clusters. Even in these latter instances, we attributed the entire $\Delta\mu$ to the $\mu_o'\chi_{\mathrm{Pt\text{-}H}}$ contribution [2]. Ankudinov *et al.* [1] correctly point out that the changing Fano-like profile in these latter instances arises from the changing relative size of the three contributions. We show here that the final profile depends strongly on the adsorption site, and therefore the claim that the first two terms in $\Delta\mu$ generally dominate [1] is not justified for supported small Pt particles such as those found in most active catalysts.

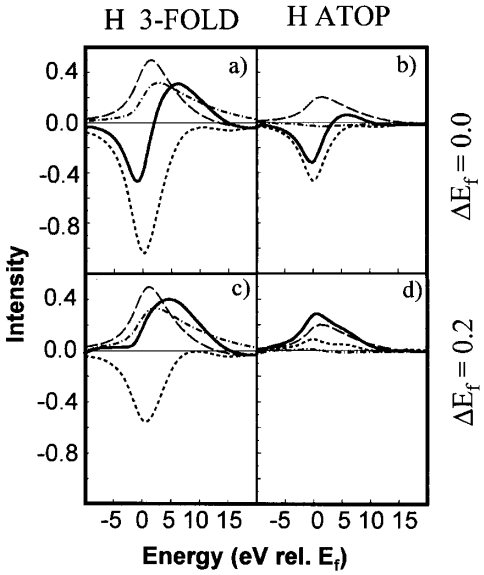

FIG. 1. FEFF8 results for (a) threefold, Pt_6H_8 and (b) atop, Pt_6H_6 adsorbed H. Calculations in (c) and (d) have the Fermi level shifted up by 0.2 eV. $\Delta\mu = \mu(Pt_6H_x) - \mu(Pt_6)$ (solid lines), $\mu_o'\chi_{\mathrm{Pt\text{-}H}}$ (dashed lines), $\Delta[\mu_o\chi_{\mathrm{Pt\text{-}Pt}}]$ (dotted lines), and $\Delta\mu_o$ (dot-dashed lines).

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