Microstructure of Bimetallic Pt–Pd Catalysts under Oxidizing Conditions


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Figures S-1, S-2, and S-3 below are the XRD patterns of all six samples in both the aged and aged plus reduced states. These patterns represent the raw data obtained from the diffractometer. The data has not been background subtracted.

**Figure S-1.** XRD patterns of aged and aged plus reduced Pt catalysts before background subtraction. To allow comparison between the catalysts, the data for each catalyst was vertically offset.

**Figure S-2.** XRD patterns of aged and aged plus reduced Pd catalysts before background subtraction. To allow comparison between the catalysts, the data for each catalyst was vertically offset.
**Figure S-3.** XRD patterns of aged and aged plus reduced Pt-Pd catalysts before background subtraction. To allow comparison between the catalysts, the data for each catalyst was vertically offset.

In the main text, the XANES plots only showed the spectra from $\gamma$-Al$_2$O$_3$, and the EXAFS plots only showed the spectra from La-Al$_2$O$_3$ to make the images easier to view. Below are the remaining XAS spectra that correspond to Figures 2, 3, 5, and 6 in the main text. These figures have data from catalysts on both the La-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ supports.

**Figure S-4(a).** XANES at the Pd edge showing that the Pd-only catalysts are fully oxidized while the bimetallics show Pd to be partly oxidized, even after aging at 750°C in air for 10 hours.
Figure S-4(b). XANES at the Pd edge after reduction in H₂, showing that the Pd is almost fully reduced in all catalysts.

Figure S-5(a). XANES at the Pt edge showing that Pt is almost fully reduced even after aging for 10 hours at 750°C in air.
Figure S-5(b). XANES at the Pt edge after H\textsubscript{2} reduction shows very little change compared to the aged samples, confirming that Pt stays metallic when treated in air at 750°C.

Figure S-6(a). Fourier Transform EXAFS Pd K edge results for the aged samples. The monometallic samples show peaks corresponding to Pd-O and a second shell Pd-Pd. The lower amplitude for the second shell is consistent with small, dispersed, PdO on the surface of the catalyst. In contrast, the bimetallic samples show peaks consistent with Pt neighbors as well as Pd neighbors for metallic Pd and only the first shell oxide, suggesting that the oxide is now a dispersed phase.
Figure S-6(b). EXAFS Pd K edge results for the aged + reduced samples. The monometallic samples show a Pd-Pd peak with no higher shells, consistent with small metal particles (which cannot be seen via XRD). The bimetallics show co-existence of the alloy and some dispersed Pd on the catalyst, as confirmed also by STEM-EDS.

Figure S-7(a). EXAFS Pt L3 edge results for the aged samples, showing very little difference between the aged samples and the reduced samples seen in figure (b).
Figure S-7(b). EXAFS Pt L3 edge results for the aged + reduced samples.

Complete Reference