Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Illuminating Surface Atoms in Nanoclusters by Differential X-ray Absorption Spectroscopy

Charles S. Spanjers,[1] Thomas P. Senftle,[1] Adri C. T. van Duin,[2] Michael J. Janik,[1] Anatoly I. Frenkel,[3]* and Robert M. Rioux[1]*

[1]*Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[2]*Department of Mechanical and Nuclear Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[3]*Physics Department, Yeshiva University, 245 Lexington Avenue, New York, New York 10016, USA*

*Authors to which correspondence should be addressed: anatoly.frenkel@yu.edu, rioux@engr.psu.edu

Derivation of Eq. (5)

The derivation of eq. (5) is provided in its entirety below.

Starting with Eq. (4) from the primary manuscript:

$$\Delta\text{-}EXAFS = \frac{S_0^2 N_s f(k) e^{-\frac{2r_1'}{\lambda(k)}} e^{-2k^2\sigma_1^2}}{kr_1'^2}\sin\left(2kr_1' + \delta(k)\right) - \frac{S_0^2 N_s f(k) e^{-\frac{2(r_1' + \Delta r)}{\lambda(k)}} e^{-2k^2\sigma_2^2}}{k(r_1' + \Delta r)^2}\sin\left(2k(r_1' + \Delta r) + \delta(k \quad (4)$$

Under the approximation that the bond length disorder does not change between the two states ($\sigma_1'^2 = \sigma_2'^2$), and that Δr << r, we get the following equation:

$$\Delta\text{-}EXAFS = \frac{S_0^2 N_s f(k) e^{-\frac{2r_1'}{\lambda(k)}} e^{-2k^2\sigma_1'^2}}{kr_1'^2}\left[\sin\left(2kr_1' + \delta(k)\right) - \sin\left(2k(r_1' + \Delta r) + \delta(k)\right)\right] \quad (4b)$$

Using the sum-to-product trigonometric identity ($\sin\alpha \pm \sin\beta = 2\sin\frac{1}{2}(\alpha \pm \beta)\cos\frac{1}{2}(\alpha \mp \beta)$), Eq. 4b becomes

$$\Delta\text{-}EXAFS = \frac{S_0^2 N_s f(k) e^{-\frac{2r_1'}{\lambda(k)}} e^{-2k^2\sigma_1'^2}}{kr_1'^2}\left[2\sin(k\Delta r)cos\left(2kr_1' + \delta(k)\right)\right] \quad (4c)$$

Since $\cos(\alpha) = -\sin\left(\alpha + \frac{\pi}{2}\right)$, equation (5) is equivalent to

$$\Delta\text{-}EXAFS = -\frac{S_0^2 N_s f(k) e^{-\frac{2r_1'}{\lambda(k)}} e^{-2k^2\sigma_1'^2}}{kr_1'^2}\left[2\sin(k\Delta r)sin\left(2kr_1' + \delta(k) + \frac{\pi}{2}\right)\right] \quad (4d)$$

For a small difference in bond length change, $\sin(k\Delta r) \sim k\Delta r$, hence,

$$\Delta\text{-}EXAFS = -\frac{S_0^2 N_s f(k) e^{-\frac{2r_1'}{\lambda(k)}} e^{-2k^2\sigma_1^2}}{kr_1'^2}(2k\Delta r)\ sin\left(2kr_1' + \delta(k) + \frac{\pi}{2}\right) \quad (5)$$

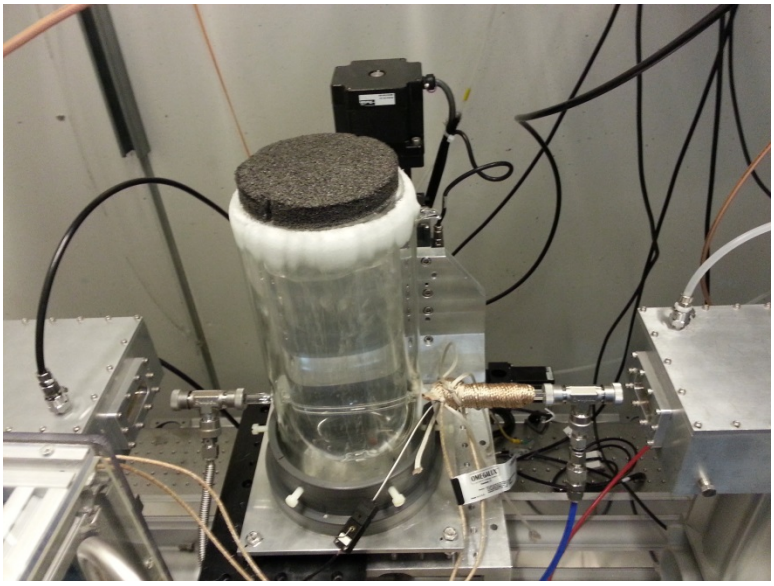

Fig. S1. Photo of specially designed *in situ* reactor. The sample is packed into the steel cylindrical holder in the center of the liquid nitrogen vacuum-insulated flask. Heating is accomplished outside the flask with heat tape and the sample can be moved from the cooled zone to the heated zone using a magnet.

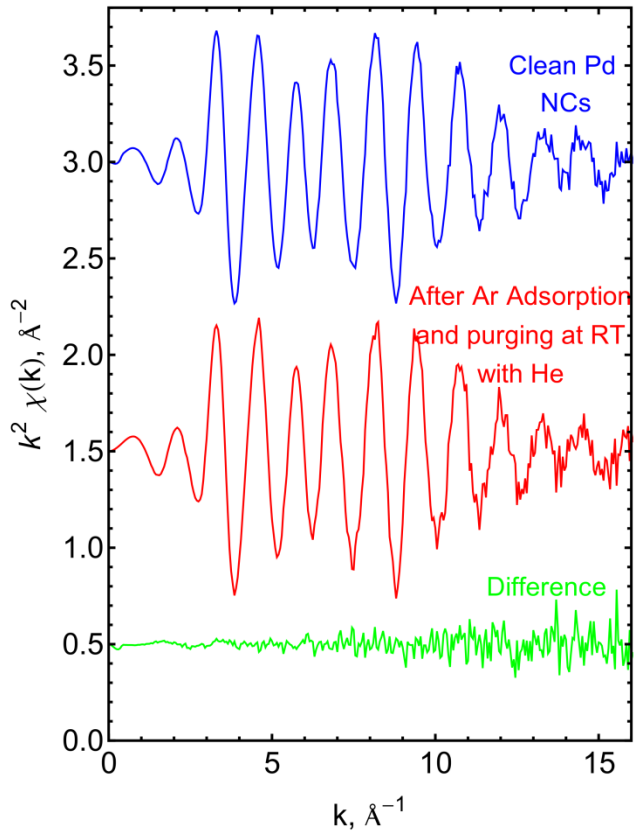

Fig. S2. k^2-weighted $\chi(k)$ EXAFS data for the clean Pd NCs and the Pd NCs after Ar adsorption and purging at room temperature (RT) with He. The difference shows no oscillatory behavior. The data are artificially offset for clarity.

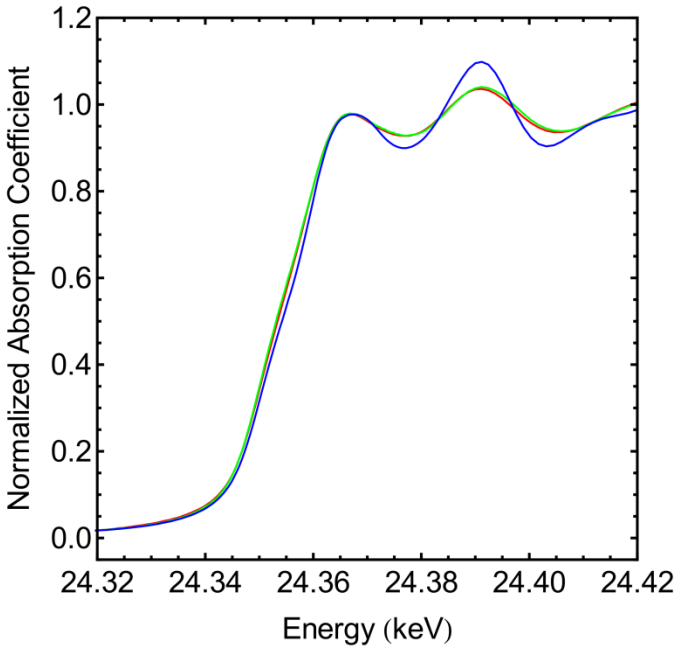

Fig. S3. XANES spectra for the clean Pd NCs (green), after Ar adsorption (red), and the reference Pd foil (blue).

Table S1. Fit parameters obtained from the differential data using a Pd-Ar scattering model.

Parameter	Value
ΔE_0	20 ± 7 eV
r	3.09 ± 0.06 Å
σ^2	-0.0009 ± 0.002
N	0.39

Table S2. Fit parameters obtained from the differential data using a Pd-Pd scattering model under the assumption the Pd-Pd coordination number changes.

Parameter	Value
ΔE_0	0 ± 2 eV
r	2.82 ± 0.02 Å
σ^2	-0.0045 ± 0.0006
N	0.57

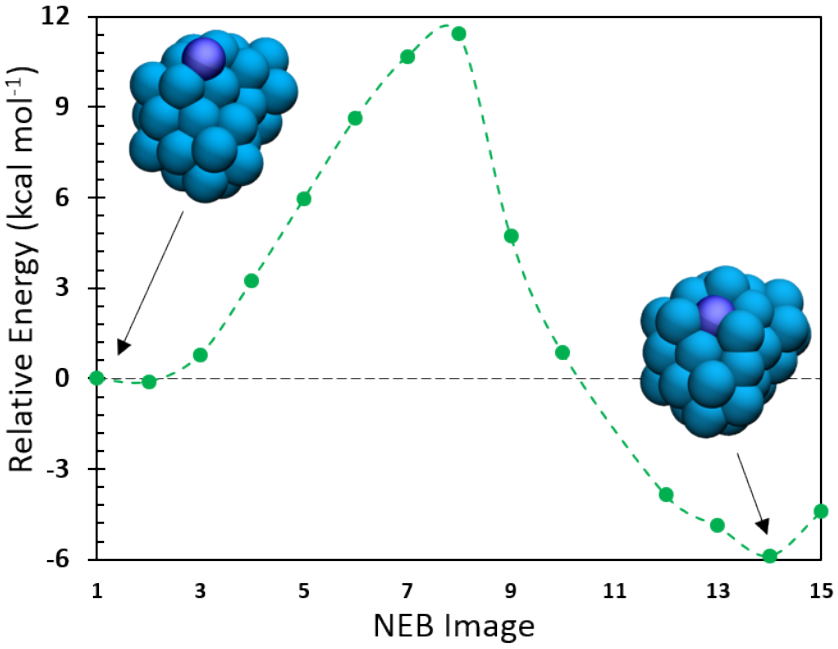

Fig. S4. ReaxFF-NEB barrier for surface reconstruction. Insets depict the initial and final cluster structures where the NEB images were obtained by linear interpolation of the atomic coordinates.

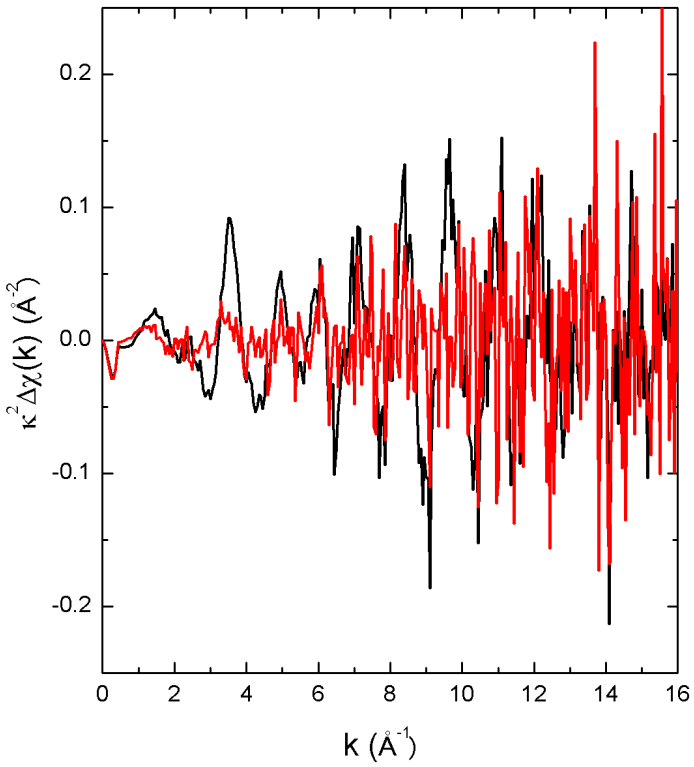

Fig S5. Differential EXAFS spectra for two different sets of data for the Pd/SiO_2 catalyst. The first set of data corresponds to experimental data collected in He and in Ar at 77 K (black curve). The second set of data corresponds to the difference spectra between the sample in He before Ar was introduced and after it was replaced by He at 77 K (red curve).