Supplementary Information for
"Real Time Indirect Nanoplasmonic in situ Spectroscopy of Catalyst Nanoparticle Sintering"

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1. Stability of a blank INPS sensor in 4% O_2 at 610 °C

Figure S1 comprises a control experiment where a blank INPS sensor (i.e., Au nanoparticles, covered by a SiO_2 layer, without Pt nanoparticles) is exposed to oxidizing atmosphere as during a sintering experiment. Clearly, no significant shift of the centroid occurs during the entire 6-hour exposure. This measurement is thus another very strong indicator that the measured centroid shifts in oxidizing atmosphere with Pt nanoparticles on the INPS sensor clearly and directly are related to the sintering of the Pt catalyst and not to an interaction with the environment of the sensor itself.

2. Sintering kinetics

Figure S2 shows how the calculated (from $\Delta\lambda$) particle-diameter changes as a function of time during exposure to oxidizing atmosphere at four different temperatures, i.e. during the sintering process. The shown data are the ones used to generate the $\log(D)$-$\log(t)$ plot in Figure 6 in the main text.

3. Theoretical background

The kinetics of sintering of metal nanoparticles can be fitted by using the phenomenological equation for the average particle radius,

$$\frac{d\langle R\rangle}{dt} = \frac{A}{\langle R\rangle^{n-1}}, \qquad (1)$$

where n and A are adjustable parameters. This equation yields $\langle R \rangle^n = \langle R \rangle_\circ^n + nAt$, or

$$\langle R \rangle = (\langle R \rangle_\circ^n + nAt)^{1/n}, \tag{2}$$

where $\langle R \rangle_\circ$ is the initial value of the average radius. Asymptotically (at $At \gg \langle R \rangle_\circ^n$), Eq. (2) predicts power-law growth,

$$\langle R \rangle \propto t^{1/n}. \tag{3}$$

This law was widely employed to fit and/or interpret experimental results.

Eqs. (1)-(3) are valid in the framework of the conventional models of the LSW type for Ostwald ripening and the models assuming the sintering to occur via nanoparticle diffusion (for the references, see the main text). The former models are based on the use of the Kelvin equation including surface energy or tension, γ (in our context, these terms can be employed interchangeably). Specifically, the conventional treatments are based on the assumption that $2\gamma v/(k_{\mathrm{B}}TR) \ll 1$, where v is the atomic volume. For the metal nanoparticles under consideration, this condition does not hold. The Kelvin equation is, however, applicable and can be employed to scrutinize sintering kinetics as outlined below. At present, one can find more accurate treatments of the energetics of bare metal nanoparticlles (see, e.g., Refs. [9] and [16] in the main text). In our case, the Pt particles are covered by oxide, and their shape is not well established. Under such circumstances, the use of more accurate equations is now hardly possible, because such equations are lacking.

Let us consider that the sintering of supported metal nanoparticles is kinetically limited and occurs via 2D detachment, surface diffusion, and attachment of metal atoms (in the metallic or oxidized state). In this case, the balance equation for the number of atoms, N, in a particle is

$$dN/dt = W_{\mathrm{a}} - W_{\mathrm{d}}, \tag{4}$$

where W_{a} and W_{d} are the attachment and detachment rate. To rewrite Eq. (1) in terms of the particle radius, we consider that the particle shape is close to hemispherical (for a truncated sphere, the analysis and final results are similar) and take into account that $N = 2\pi R^3/(3v)$, where $2\pi R^3/3$ is the particle volume. Substituting this expression for N into Eq. (4) yields

$$\frac{2\pi R^2}{v}\frac{dR}{dt} = W_{\mathrm{a}} - W_{\mathrm{d}}. \tag{5}$$

According to the Kelvin equation, the contribution of the surface energy to the detachment activation energy is $\Delta E = -2\gamma v/(k_{\mathrm{B}}TR)$, and accordingly the detachment rate can be represented as

$$W_{\mathrm{d}} = \frac{2\pi R\nu}{a}\exp\left(-\frac{E_\circ - 2\gamma v}{k_{\mathrm{B}}TR}\right), \tag{6}$$

where $2\pi R/a$ is the number of metal atoms on the metal-support-gas interface ($a = v^{1/3}$ is the atomic size), and $E_\circ$ and $\nu \simeq 10^{13}$ s^{-1} are the main size-independent part of the activation energy and the pre-exponential factor for detachment, respectively.

The attachment rate is also proportional to $2\pi R/a$ and can be calculated by using the detailed balance principle or, more specifically, taking into account that W_d and W_a should be nearly equal near the maximum of PSD, i.e., at $R = \langle R \rangle$. This condition yields

$$W_\mathrm{a} = \frac{2\pi R\nu}{a} \exp\left(-\frac{E_\circ - 2\gamma v}{k_\mathrm{B}T\langle R\rangle}\right). \tag{7}$$

Substituting (6) and (7) into (5) results in

$$\frac{dR}{dt} = \frac{B}{R}\left[\exp\left(\frac{2\gamma v}{k_\mathrm{B}T\langle R\rangle}\right) - \exp\left(\frac{2\gamma v}{k_\mathrm{B}TR}\right)\right], \tag{8}$$

where $B = a^2\nu \exp(-E_\circ/k_\mathrm{B}T)$. The equations of this type were already used in the literature (see, e.g., Ref. [9] in the main text).

In the models of the LSW type, as already noted, $2\gamma v/(k_\mathrm{B}TR)$ is considered to be small, and the corresponding exponential functions [like those in Eq. (8)] are expanded as $\exp(x) \simeq 1 + x$. In our case, this expansion may fail. To get a better approximation, Eq. (8) can be rewritten as

$$\frac{dR}{dt} = \frac{B}{R}\exp\left(\frac{2\gamma v}{k_\mathrm{B}T\langle R\rangle}\right)\left\{1 - \exp\left[\frac{2\gamma v}{k_\mathrm{B}T}\left(\frac{1}{R} - \frac{1}{\langle R\rangle}\right)\right]\right\}. \tag{9}$$

Taking into account that for the main part of a PSD the argument of the second exponential function in Eq. (9) is appreciably smaller than that of the first one and expanding only the second exponential function, we obtain

$$\frac{dR}{dt} = \frac{A}{R^2}\exp\left(\frac{2\gamma v}{k_\mathrm{B}T\langle R\rangle}\right)\left(\frac{R}{\langle R\rangle} - 1\right), \tag{10}$$

where $A = 2\gamma v B/k_\mathrm{B}T = (2\gamma a^5\nu/k_\mathrm{B}T)\exp(-E_\circ/k_\mathrm{B}T)$.

If the PSD during the growth is self-similar, the dimensionless ratio in the second parentheses (i.e. $R/\langle R\rangle - 1$) in Eq. (10) remains constant inside the PSD, and the scale of the rate of the growth of the average radius is determined by the terms before those parentheses. Thus, the equation for $\langle R \rangle$ can approximately be represented as

$$\frac{d\langle R\rangle}{dt} = \frac{A}{\langle R\rangle^2}\exp\left(\frac{2\gamma v}{k_\mathrm{B}T\langle R\rangle}\right). \tag{11}$$

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If $2\gamma v/(k_{\mathrm{B}}TR) \ll 1$, the exponential function is here close to unity, and, as expected, this equation becomes equivalent to Eq. (1) with $n = 3$.

We have fitted our kinetics (see, e.g., Figure S3) by using Eq. (1) and considering A and n to be adjustable parameters. The corresponding exponent, $n = 5$, is found to be larger than those ($n = 3$ or 4) predicted for 2D Ostwald ripening by the conventional models of the LSW type, and accordingly it could be interpreted as the process occurring via nanoparticle diffusion.

Alternatively, we have used Eq. (11) (see Figure S3 and Figure 6 in the main text) considering A and γ to be adjustable parameters. The suitable value of γ is found to be 1.5 J/m^2. As expected, this value is somewhat lower than the surface energy for Pt (2-3 J/m^2 [1,2]), because the detachment is facilitated by oxygen. Scrutinizing the temperature dependence of A, we have found that $E_\circ = 364$ kJ/mol. As expected, this detachment activation energy is lower than the Pt sublimation energy (557 kJ/mol) for the same reason. For comparison, we mention that the detachment activation energy, obtained in studies of sintering of Au nanoparticles on TiO$_2$, is reported to be 327 kJ/mol (see Ref. [16] in the main text).

As noted in the main text, the fit by using Eq. (11) is preferable. Here, we add that the example shown in Figure S3 clearly indicates that the formal fit by employing the simplest power-low equation (1) may easily be misleading.

References

[1] Foiles, S.M., Baskes, M.I. & Daw, M.S., Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys. *Physical Review B* **33**, 7983-7991 (1986).

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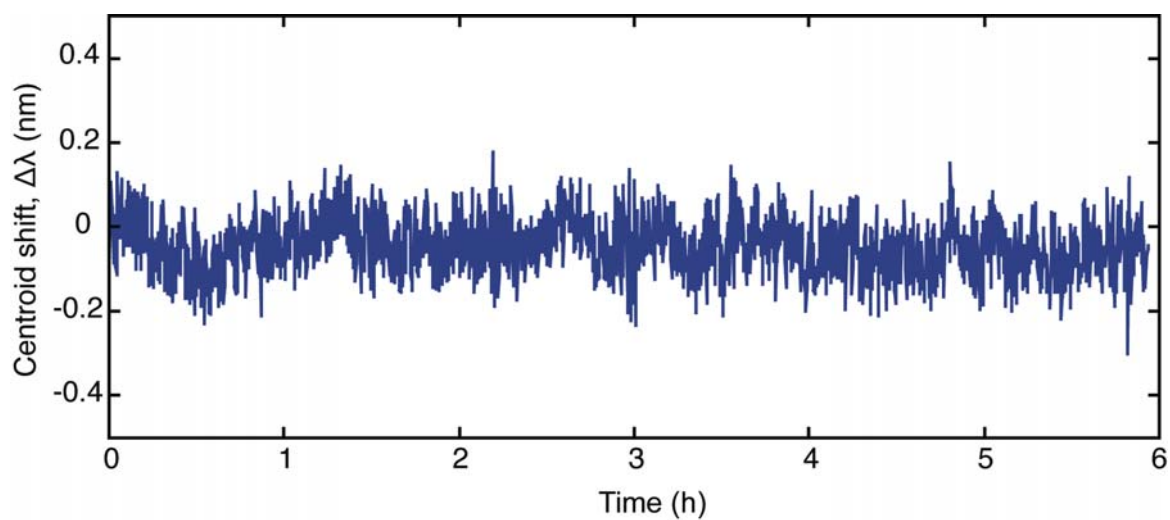
Supplementary Figures

Figure S1: Centroid shift, $\Delta\lambda$, during 6 h exposure of a blank INPS sensor to 4%O_2 in Ar at 610°C.
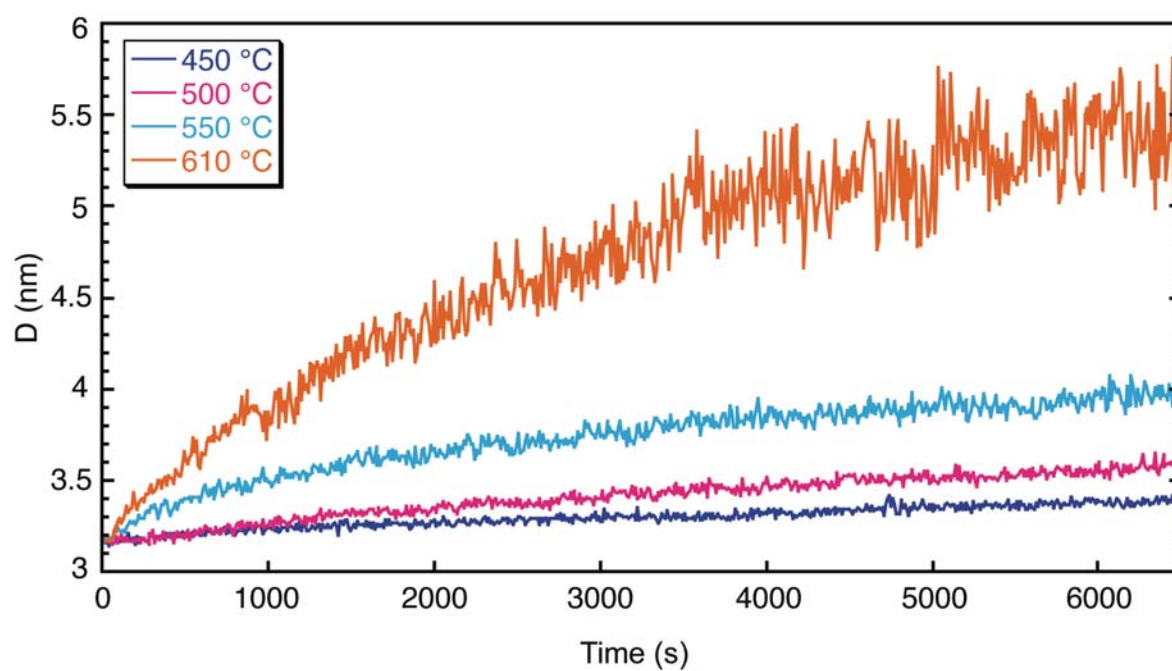

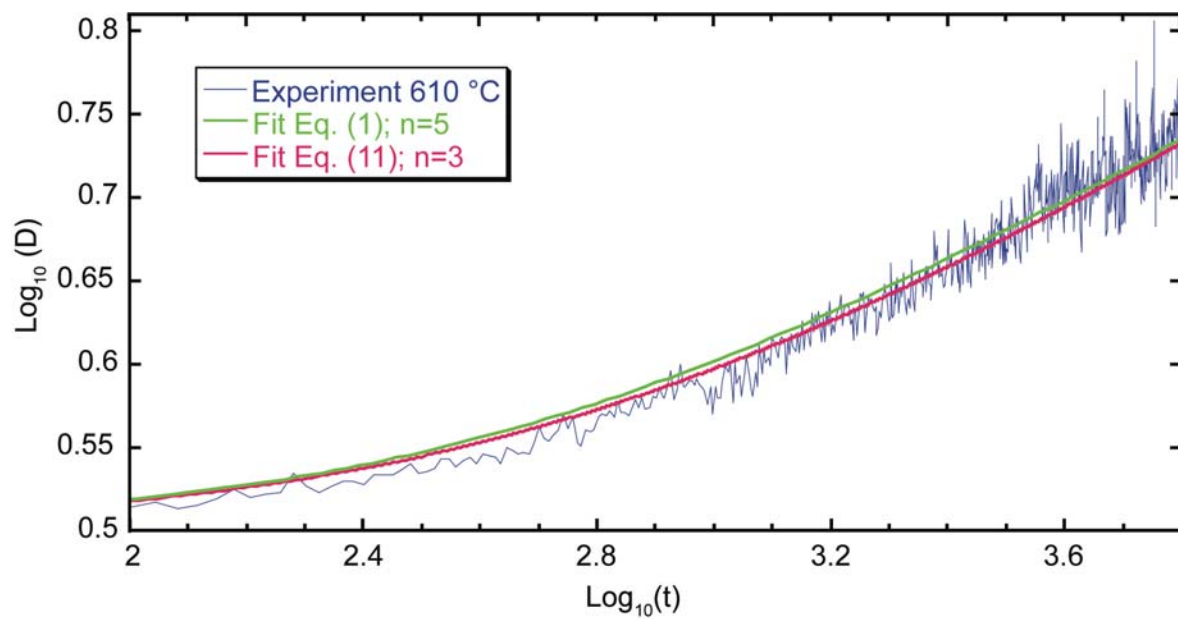**Figure S2:** INPS Sintering kinetic curves for 4 different temperatures.

Figure S3: Quantitative analysis of INPS kinetics of Pt/SiO$_2$ sintering at 610 C. The upper (green) solid line shows the fit of the experimental data by using Eq. (1) with *n*=5. The lower (pink) solid line corresponds to the fit by employing Eq. (11) with *n*=3.