Electronic Supplementary Information

Shape-Persistent Porous Organic Cage Supported Palladium Nanoparticles as Heterogeneous Catalytic Materials

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This file contains:

- Experimental Details
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- Additional data and characterization results
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- References
**Table S1.** Synthesis of Pd(NO\(_3\))\(_2\)@CC3 crystals with various nominal Pd loadings

| Pd(NO\(_3\))\(_2\) loading (wt.% Pd(NO\(_3\))\(_2\)) | Mass of CC3 | Volume of Pd(NO\(_3\))\(_2\) stock solution used for Pd(NO\(_3\))\(_2\)@CC3 cocrystals (3 mg/ml) |
|--------------------------------------------------|-------------|----------------------------------------------------------------------------------|
| 1 wt.% Pd(NO\(_3\))\(_2\) loading                | 10 mg       | 30 µL                                                                             |
| 2 wt.% Pd(NO\(_3\))\(_2\) loading                | 10 mg       | 60 µL                                                                             |
| 4 wt.% Pd(NO\(_3\))\(_2\) loading                | 10 mg       | 120 µL                                                                            |
| 8 wt.% Pd(NO\(_3\))\(_2\) loading                | 10 mg       | 240 µL                                                                            |

**Table S2.** Pd loadings verified by ICP-OES

| Pd(NO\(_3\))\(_2\) loading (wt.% Pd(NO\(_3\))\(_2\)) | Expected / calculated wt.% Pd based on precursor amount. | Wt.% Pd obtained from ICP-OES data. |
|--------------------------------------------------|----------------------------------------------------------|-------------------------------------|
| 1                                                | 0.46                                                     | 0.5                                 |
| 2                                                | 0.92                                                     | 1                                   |
| 4                                                | 1.8                                                      | 2                                   |
| 8                                                | 3.7                                                      | 4                                   |

**X-ray Absorption Spectroscopy (XAS) – further details of processing methods.**

XANES spectra were aligned by calibration of the first zero crossing point of the second derivative of the Pd foil reference spectra in each case. XAFS data processing was performed using IFEFFIT\(^1\) with the Horae package\(^2\) (Athena and Artemis). The amplitude reduction factor,
$S_0^2$ was derived from EXAFS data analysis of the Pd foil reference spectrum (for which the co-
ordination numbers of the fcc metal are known), yielding a value of 0.87±0.04. This was then
fixed in the analysis of sample spectra. The parameters corresponding to the correction to the
photoelectron energy origin, co-ordination numbers, bond lengths, and mean-squared
relative deviation of atoms around absorbing atoms were then varied during fitting. Two small
heteroatom environments (based on nearest neighbour oxygen and nitrogen in crystalline
Pd(NO$_3$)$_2$) and the Pd-Pd nearest neighbour distance in fcc metal were considered as possible
contributions for first shell fits. The number of variables was kept to a minimum by making
the physically reasonable assumption that the mean-squared relative deviation of the two
small heteroatom neighbours is the same (the primary conclusion of the fits in which this is
the case is that there is no significant contribution from Pd-Pd interactions). These fits are
shown in Figure S7 and Table S4. All fits were performed using multiple k-weight fitting,
although $k^3$-weighted data is shown in figures. Improved fits of the reference metal foil (Figure
S8, Table S5) and the sample treated at 200 °C containing small nanoparticles (Figure S9, Table
S5) were obtained by fitting to higher values of $R$ using a model accounting for multiple
scattering paths (those regarded significant in Feff) up to 5 Å effective path length, and using
the further physically reasonable assumption that all Pd-Pd interactions grow or shrink by a
constant scaling factor relative to the known bulk Pd fcc metal crystal. Assumed relations of
co-ordination number and mean-squared relative deviation are tabulated in Table S3.

Table S3. Assumed relations of co-ordination number and mean-squared relative deviation
used in extended Pd fits (based on fcc structure).

| Scattering path                  | Co-ordination number | $\sigma^2$     |
|---------------------------------|----------------------|----------------|
| Pd1 Single scattering           | 12                   | $\sigma^2$(Pd1) |
| Pd2 Single scattering           | 6                    | $\sigma^2$(Pd2) |
| Pd1Pd1 Acute triangle           | 48                   | $2 \times \sigma^2$(Pd1) |
| Pd1Pd2 Other double scattering  | 48                   | $\sigma^2$(Pd1) + $\sigma^2$(Pd2) |
| Pd 3 Single scattering          | 24                   | $\sigma^2$(Pd3) |
| Pd1Pd1 Obtuse triangle           | 48                   | $2 \times \sigma^2$(Pd1) |
| Pd1Pd3 Obtuse triangle           | 96                   | $\sigma^2$(Pd1) + $\sigma^2$(Pd3) |
| Pd4 Single scattering           | 12                   | $\sigma^2$(Pd4) |
| Pd1Pd1 Non-forward linear       | 12                   | $2 \times \sigma^2$(Pd1) |
| Pd1Pd4 Forward scattering       | 24                   | $\sigma^2$(Pd4) |
| Pd1 Forward through absorber    | 12                   | $2 \times \sigma^2$(Pd1) |
| Pd1Pd4Pd1 Double forward scattering | 12            | $\sigma^2$(Pd4) |

*To minimise the number of independent parameters the approximation is made that $CN_{Pd1Pd1}$ can be used when fitting all three of these paths involving two nearest shell Pd scatterers and the 4:4:1 ratio maintained.*
Additional data and characterization results

Figure S1. A structural model of Pd(NO$_3$)$_2$ fitting inside CC3.

Figure S2. TEM images of Pd NPs / CC3 produced from Pd(acac)$_2$ showing much lower degree of particle size control obtained.
Figure S3. (a) $^1$H NMR spectrum (CDCl$_3$) of CC3-R. (b) $^{13}$C NMR spectrum (CDCl$_3$) of CC3-R.
Figure S4. $^1$H NMR spectra for pure CC3, 0.5 wt.% Pd(NO$_3$)$_2$@CC3, this sample after H$_2$ reduction at 150 °C for 1 hour, and 0.5 wt.% Pd NPs@CC3 (the sample formed after H$_2$ reduction at 200 °C for 1 hour). It should be noted peaks at 0.88 and 1.26, and 1.56 ppm are due to contaminants during processing (silicone grease, grease and water respectively), and so no discernible changes are seen in the spectra obtained.
**Figure S5.** Photographs showing the relative colours of (a) CC3; (b) Pd(NO$_3$)$_2$@CC3 as prepared; (c) Pd(NO$_3$)$_2$@CC3 after reduction at 150 °C and (d) Pd(NO$_3$)$_2$@CC3 after reduction at 200 °C (referred to as PdNP@CC3).

**Figure S6.** Normalised XANES spectra (a) near and (b) expanded (as in main text) at the Pd K-edge for Pd reference foil, Pd(NO$_3$)$_2$@CC3 before reduction and after reduction in 10% H$_2$ at 150 °C and 200 °C (Pd NPs@CC3). The photon energy scale has been corrected by alignment of concurrently measured Pd foil data.
**Figure S7.** EXAFS spectroscopy data and first shell fits of Pd(NO$_3$)$_2$@CC3 untreated (left), after H$_2$ reduction at 150 °C (middle) and Pd NPs@CC3 formed after H$_2$ reduction at 200 °C (right), showing (a, d, g) k-space and (b,e,h) magnitude R-space fits, along with (c,f,i) the real part of the R-space fit and component path contributions used listed in order of increasing effective R-distance. Fit parameters and information shown in Table S4.
**Table S4.** EXAFS fitting parameters for the Pd K-Edge plots shown in Figure S6.a

| refined parameter | Pd(NO$_3$)$_2$@CC3 | Pd(NO$_3$)$_2$@CC3 after H$_2$ 150 °C | Pd NPs@CC3 (after H$_2$ 200 °C) |
|-------------------|---------------------|---------------------------------|----------------------------------|
| $\Delta E_0$      | 11(3)               | 7(2)                            | -7.6(9)                          |
| CN$_{Pd-Pd}$      | †                   | †                               | 5.1(7)                           |
| CN$_{Pd-X1}$      | 2.8(7)              | 3.0(5)                          | 2.5(1.0)                         |
| CN$_{Pd-X2}$      | 1.5(1.1)            | 1.3(8)                          | †                                |
| R$_{Pd}$          | †                   | †                               | 2.738(07)                        |
| R$_{X1}$          | 2.015(4)            | 2.014(14)                       | 1.974(16)                        |
| R$_{X2}$          | 2.85(5)             | 2.85(6)                         | †                                |
| $\sigma^2_{Pd}$   | †                   | †                               | 0.009(1)                         |
| $\sigma^2_X$      | 0.002(3)            | 0.003(2)                        | 0.010(5)                         |
| goodness of fit   |                     |                                 |                                  |
| R-factor          | 0.04                | 0.04                            | 0.02                             |

| fitting range     |                     |                                 |                                  |
| k-range           | 3.0 – 9.6           | 3.0 – 12.0                      | 3.0 – 11.7                       |
| R-range           | 1.0 – 3.0           | 1.0 – 3.0                       | 1.0 – 3.0                        |
| No. of independent points | 8     | 11                          | 11                                |
| No. of fitted parameters | 6      | 6                           | 7                                |

*aFitting parameters: $S_0^2 = 0.87$ as determined by the use of a Pd foil standard; X1 and X2 denote small heteroatoms at two fixed co-ordination distances, based initially on the nearest neighbour oxygen and nitrogen in Pd(NO$_3$)$_2$; $\sigma^2_X$ is taken to be the mean-squared relative deviation for both X1 and X2. Parameters marked † belong to components producing a less good or unphysical fit when included, indicating they do not contribute significantly to the spectra (in the case of Pd-X2, this component did not contribute significantly to PdCC3 H$_2$ 200 °C because it is overwhelmed by the strength of the Pd-Pd interaction, but the lack of a fit for them doesn’t imply they are not physically present).*
Figure S8. Fit to extended R space region for Pd foil reference used to determine $S_0^2$, showing (a)k-space and (b) magnitude R-space fits, along with (c) the real part of the R-space fit and component path contributions listed in order of increasing effective R-distance. Fit parameters and information shown in Table S5. As discussed in the methods section, the extended fit was conducted to improve the reliability for the two metallic fits to account for multiple scattering and longer paths.
Figure S9. Fit to extended R space region for PdCC3 H₂ 200 °C, showing (a) k-space and (b) magnitude R-space fits, along with (c) the real part of the R-space fit and component path contributions listed in order of increasing effective R-distance. Fit parameters and information shown in Table S5. As discussed in the methods section, the extended fit was conducted to improve the reliability for the two metallic fits to account for multiple scattering and longer paths.
Table S5. Fit to extended R space region for PdCC3 H₂ 200 °C and Pd metal corresponding to Figures S8 and S9. As discussed in the methods section, the extended fit was conducted to improve the reliability for the two metallic fits to account for multiple scattering and longer paths.

| refined parameter | PdCC3 H₂ 200 °C | Pd metal foil |
|-------------------|-----------------|--------------|
| S₀²               | Fixed @ 0.87    | 0.87(4)      |
| ΔE₀               | -8.0(7)         | 3.8(3)       |
| Pd lattice expansion factor | -0.0051(19) | -0.0027(7) |
| σᵥPd₁             | 0.0092(9)       | 0.0058(3)    |
| σᵥPd₂             | 0.020(11)       | 0.0097(17)   |
| σᵥPd₃             | 0.024(15)       | 0.0096(08)   |
| σᵥPd₄             | Not included b | 0.011(3)     |
| σᵥX               | 0.006(4)        | Not included c |
| RX                | 1.969(14)       | Not included c |
| CNₐ              | 2.4(0.8)        | Not included c |
| CNPd₁             | 5.3(6)          | Fixed = 12   |
| CNPd₂             | 4.8(4.5)        | Fixed = 6    |
| CNPd₃             | 10(9)           | Fixed = 24   |
| CNPd₁xPd₁         | 35(20)          | Fixed = 48   |

**goodness of fit**

| R-factor | 0.01 | 0.01 |
| fitting range |
| k-range  | 3.0 – 11.9 | 3.0 – 14.2 |
| R-range  | 1.5 – 4.7 | 1.0 – 5.0 |
| No. of independent points | 18 | 28 |
| No. of fitted parameters | 12 | 7 |

a Fitting parameters: S₀² = 0.87 was used for the PdCC3 H₂ 200 °C sample as determined by the use of a Pd foil standard; X denotes a small heteroatom at fixed co-ordination distance Rₓ, based initially on the nearest neighbour oxygen in Pd(NO₃)₂.
b A fourth shell Pd contribution was not included as significantly outside the R-range employed in the fit.
c The heteroatom contribution was not included in the fit to the pure metal foil as there should not be significant oxidation in the bulk material.

Figure S10. SEM image of 0.5 wt.% Pd NPs@CC3 showing octahedral shaped crystals.
**Figure S11.** Bright field (left) and dark field (right) STEM images of 1 wt.% Pd NP@CC3 catalyst to show small NPs embedded into CC3 for a higher loading sample than those shown in main text.

**Figure S12.** Nitrogen adsorption (solid symbols) and desorption (open symbols) at 77 K for CC3 (black) and the 0.5 wt.% Pd NPs@CC3 (blue).
Figure 13. FTIR spectra for CC3 (black), 2 wt.% Pd(NO$_3$)$_2$@CC3 (red), and 2 wt.% Pd NPs@CC3 after H$_2$ reduction at 200 °C for 1 hour (blue). Note a higher loading was used in this case to ensure any differences should be more pronounced in the resulting spectra.
Figure S14. An enlarged view of PXRD patterns (main text Figure 4) of CC3 (black), desolvated 0.5 wt.% Pd(NO$_3$)$_2$@CC3 (blue) and 0.5 wt.% Pd NPs@CC3 after H$_2$ reduction at 200 °C (pink). The features at 7.6 °, 11 ° and 19.5 ° in both 0.5 wt.% Pd(NO$_3$)$_2$@CC3 and 0.5 wt.% Pd NPs@CC3 after H$_2$ reduction could be due to a minor R3 second polymorph.

Figure S15. PXRD of pure CC3 re-crystallized from DCM / acetone without Pd(NO$_3$)$_2$ under conditions corresponding to those used when Pd(NO$_3$)$_2$ is added, confirming the additional reflections seen with Pd(NO$_3$)$_2$ are not due to the DCM/acetone mixture (10 mg CC3 recrystallized from 2 mL DCM and 500 µL acetone).
Figure S16. (a) The Pd_{104} cluster model to represent the average nanoparticle size of 1.6 nm; (b) the size of cage molecule is 20 Å indicating the overall size of CC3 molecule (rather than the internal cage) is comparable to Pd NPs; (c) the internal cavity of a cage is 8.4 Å in diameter; (d) the pore cavity between a pair of cage molecules is 8 Å.
Figure S17. Repeat cycling of the catalyst as a function of temperature showing little change in the measured conversion (3% CO, 15% O\textsubscript{2}, balance He, total flow 60 mLmin\textsuperscript{-1}; ambient pressure; 71.5 mg of 0.5 wt.% Pd catalyst). Note, the first run was conducted under a slightly higher CO:O\textsubscript{2} ratio, and has been corrected by a known partial pressure dependence).
Figure S18. TGA mass loss profile of 0.5 wt.% Pd NPs@CC3 under air flow.

Figure S19. VT-PXRD study of 0.5 wt.% Pd NPs@CC3 to determine the structural stability in the temperature range between 110 K and 500 K. All additional reflections seen at low temperature are due to diffraction by ice on the sample holder.
Figure S20. Light off data for a similar catalyst under higher flow rate conditions (150 mLmin⁻¹ and 450 mLmin⁻¹ as compared to 60 mLmin⁻¹ used for data shown in main text; 1% CO, 0.5% O₂, balance He; ambient pressure), confirming the mass transfer effects along the reactor bed are minimal.
References

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2. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* **2005**, *12* (4), 537-541.

3. Bruns, J.; Klüner, T.; Wickleder, M. S., Oxoanionic Noble Metal Compounds from Fuming Nitric Acid: The Palladium Examples Pd(NO3)2 and Pd(CH3SO3)2. *Chemistry – A European Journal* **2015**, *21* (3), 1294-1301.