

# Supporting Information

## Spatial profiling of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst during selective ammonia oxidation

Donato Decarolis<sup>†,‡,\*</sup>, Adam H. Clark<sup>#</sup>, Tommaso Pellegrinelli<sup>€</sup>, Maarten, Nachtegaal<sup>#</sup>, Evan W. Lynch<sup>§,‡</sup>, C. Richard A. Catlow<sup>†,‡, ℓ</sup>, Emma K. Gibson<sup>‡,‡</sup>, Alexandre Goguet<sup>€,\*,‡</sup>, Peter P. Wells<sup>‡,§,◇,\*</sup>

<sup>†</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

<sup>‡</sup> UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Lab, Harwell, Oxfordshire OX11 0FA, UK

<sup>#</sup> Paul Scherrer Institute, Forschungsstrasse 111, 5232, Villigen PSI, Switzerland

<sup>€</sup> Queen's University Belfast, School of Chemistry, David Keir Building, Stranmillis Rd, Belfast BT9 5AG, United Kingdom

<sup>§</sup> School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom

<sup>ℓ</sup> Department of Chemistry, University College London, 20 Gordon St., London WC1 HOAJ, UK

<sup>‡</sup> School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, United Kingdom

<sup>◇</sup> Diamond Light Source Ltd., Harwell Science and Innovation Campus, Chilton, Didcot OX11 0DE, United Kingdom.

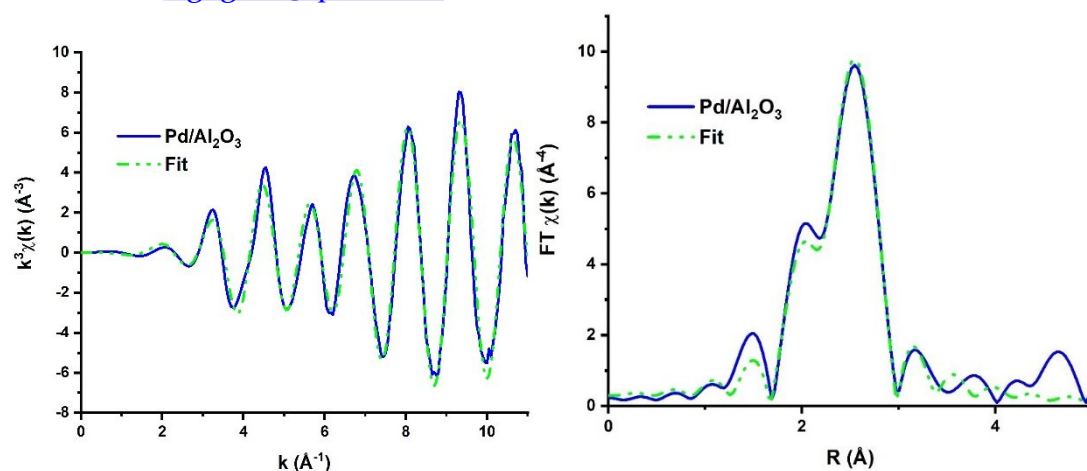
**KEYWORDS:** Ammonia oxidation, operando spectroscopy, Pd nanoparticles, SPACI-FB, heterogeneous catalysis

### Corresponding Authors

\* E-mail: [decarolisd@cardiff.ac.uk](mailto:decarolisd@cardiff.ac.uk) .

\* E-mail: [P.P.Wells@soton.ac.uk](mailto:P.P.Wells@soton.ac.uk) .

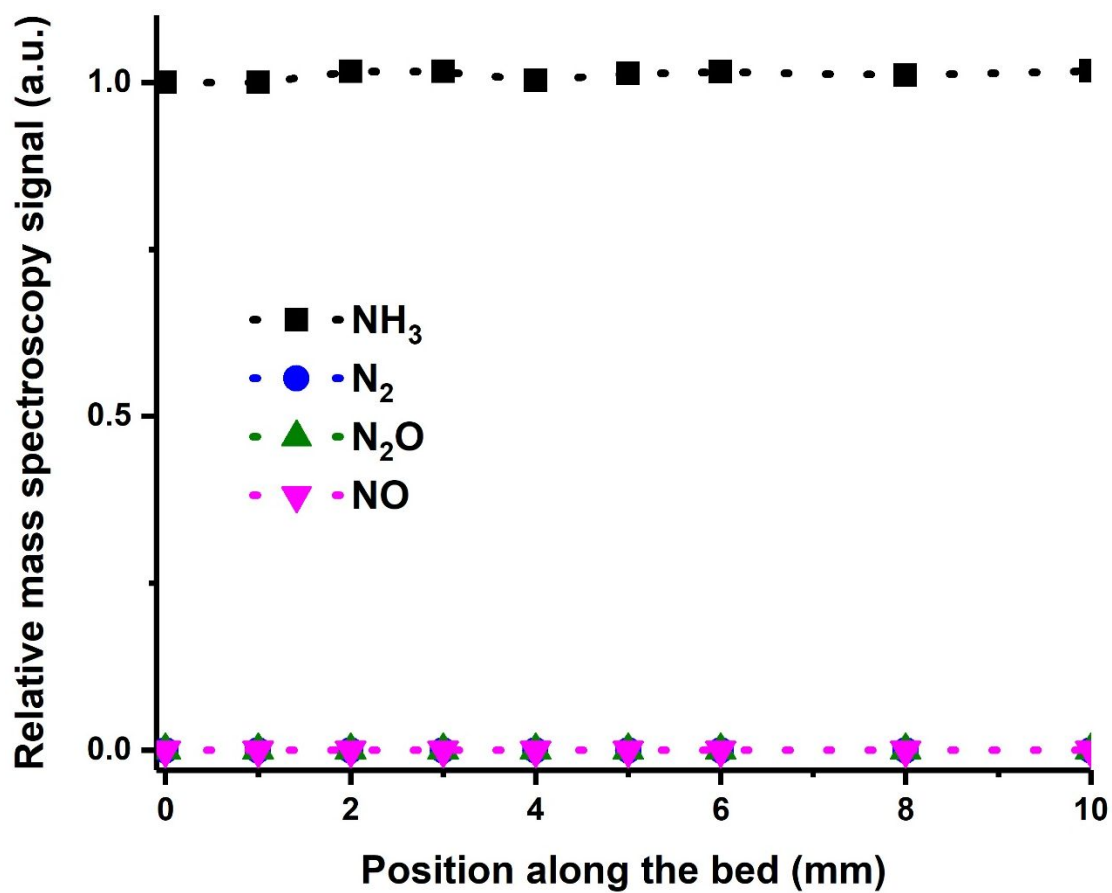
\* E-mail: [a.goguet@qub.ac.uk](mailto:a.goguet@qub.ac.uk) .



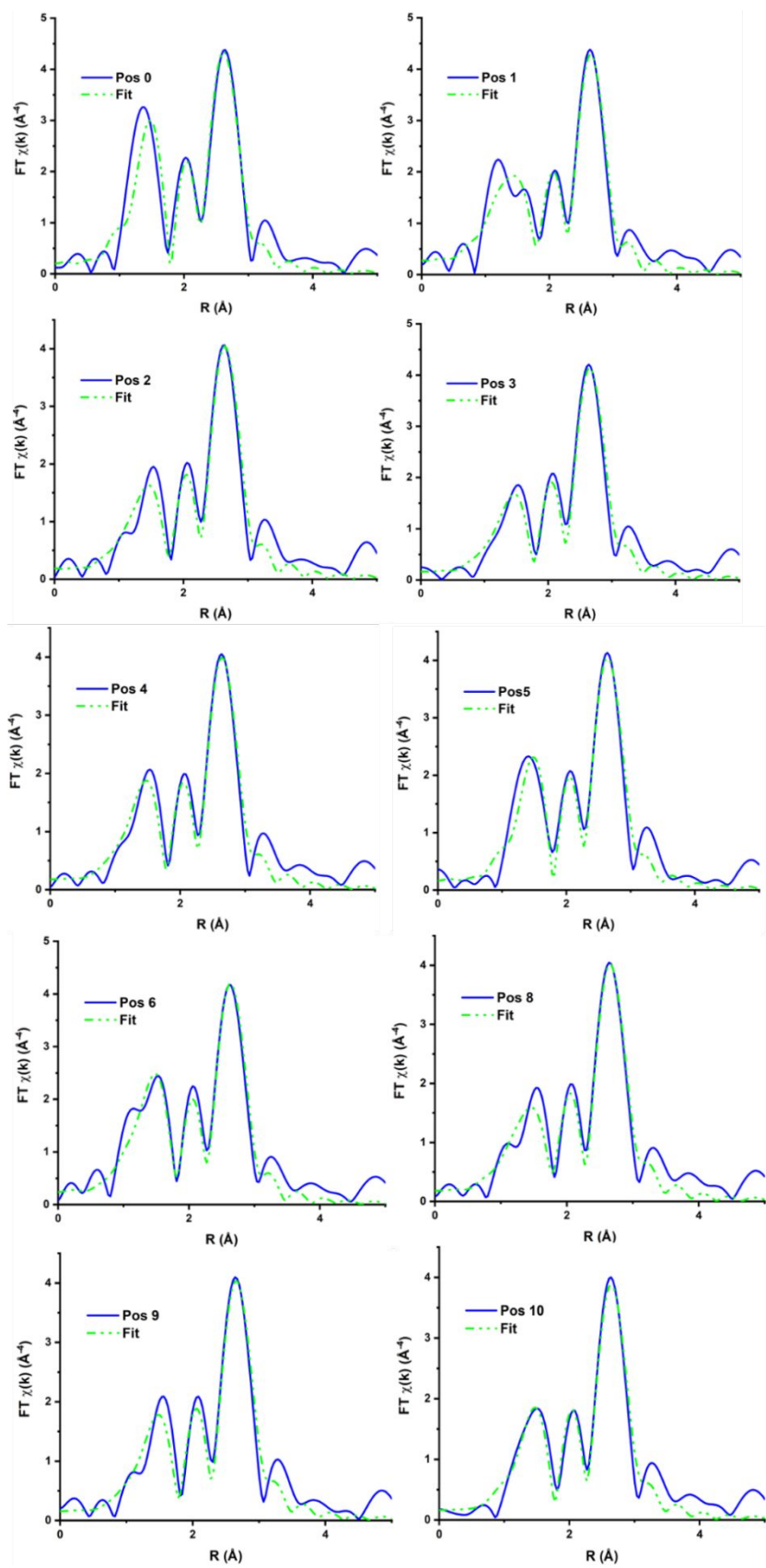
**Figure S1.** XAFS Fit of Pd/Al<sub>2</sub>O<sub>3</sub> (k-space on the left, R space on the right) after reduction

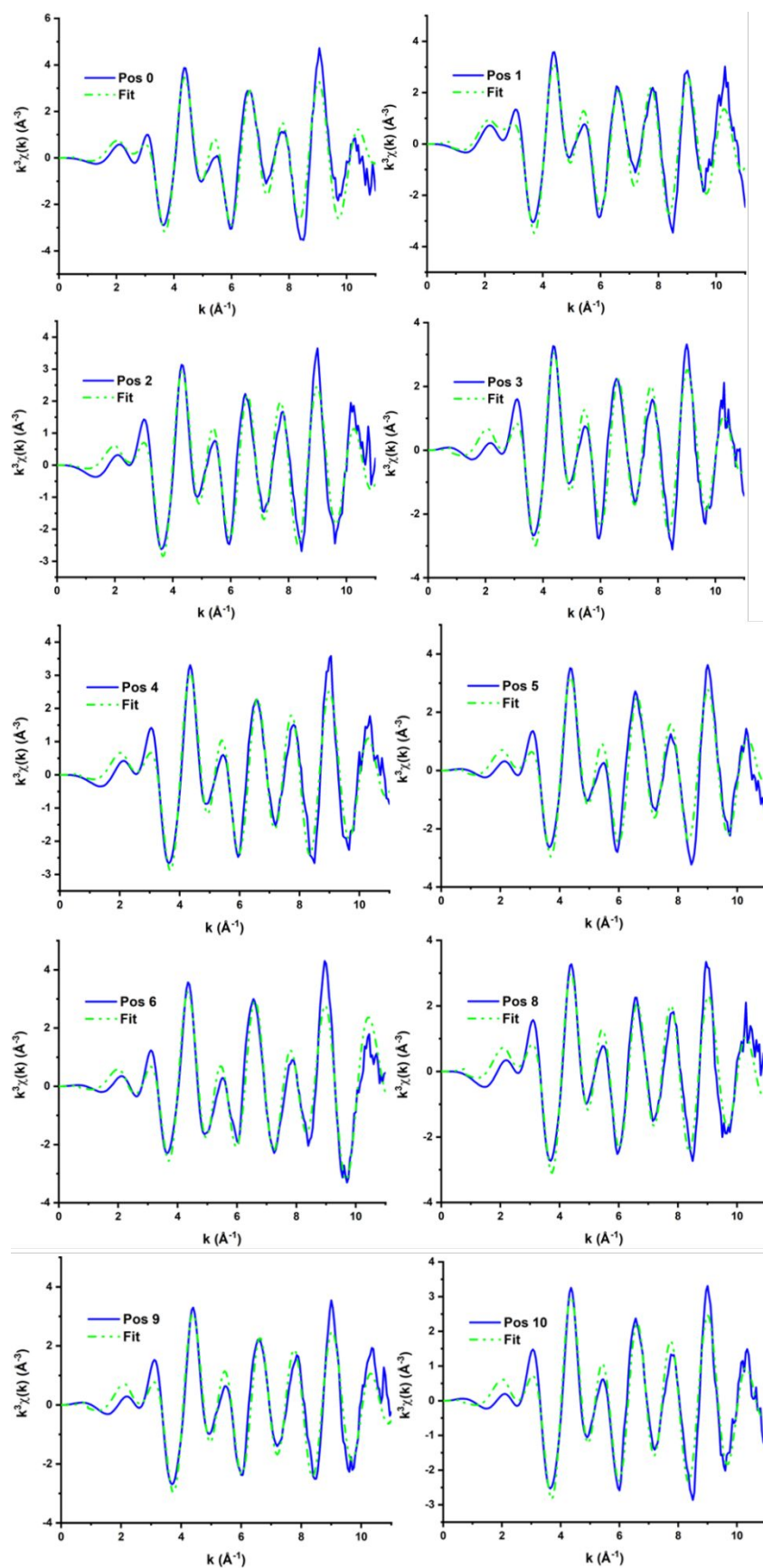
**Table S1.** XAFS Fit results for Pd/Al<sub>2</sub>O<sub>3</sub> after reduction

CN <sub>Pd-Pd</sub>	R <sub>Pd-Pd</sub> (Å)	σ <sub>Pd-Pd</sub>	ΔE	R <sub>factor</sub>
9.5 ± 0.8	2.737 ± 0.006	0.009 ± 0.0008	1.9 ± 0.6	0.012



**Figure S2.** Normalised mass spectrometry signal along the bed for Pd/Al<sub>2</sub>O<sub>3</sub> at 100 °C under reaction conditions.

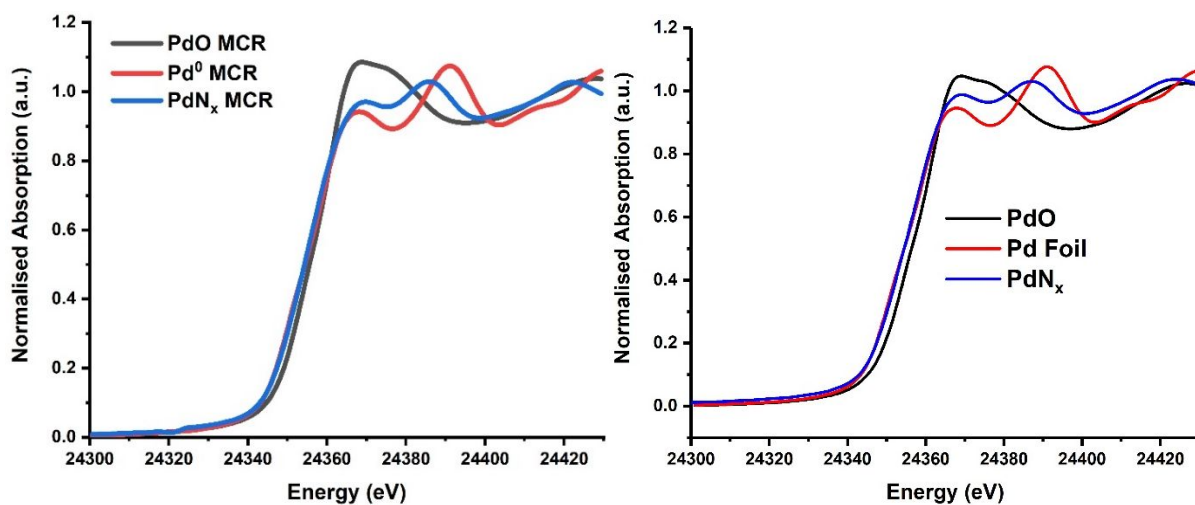




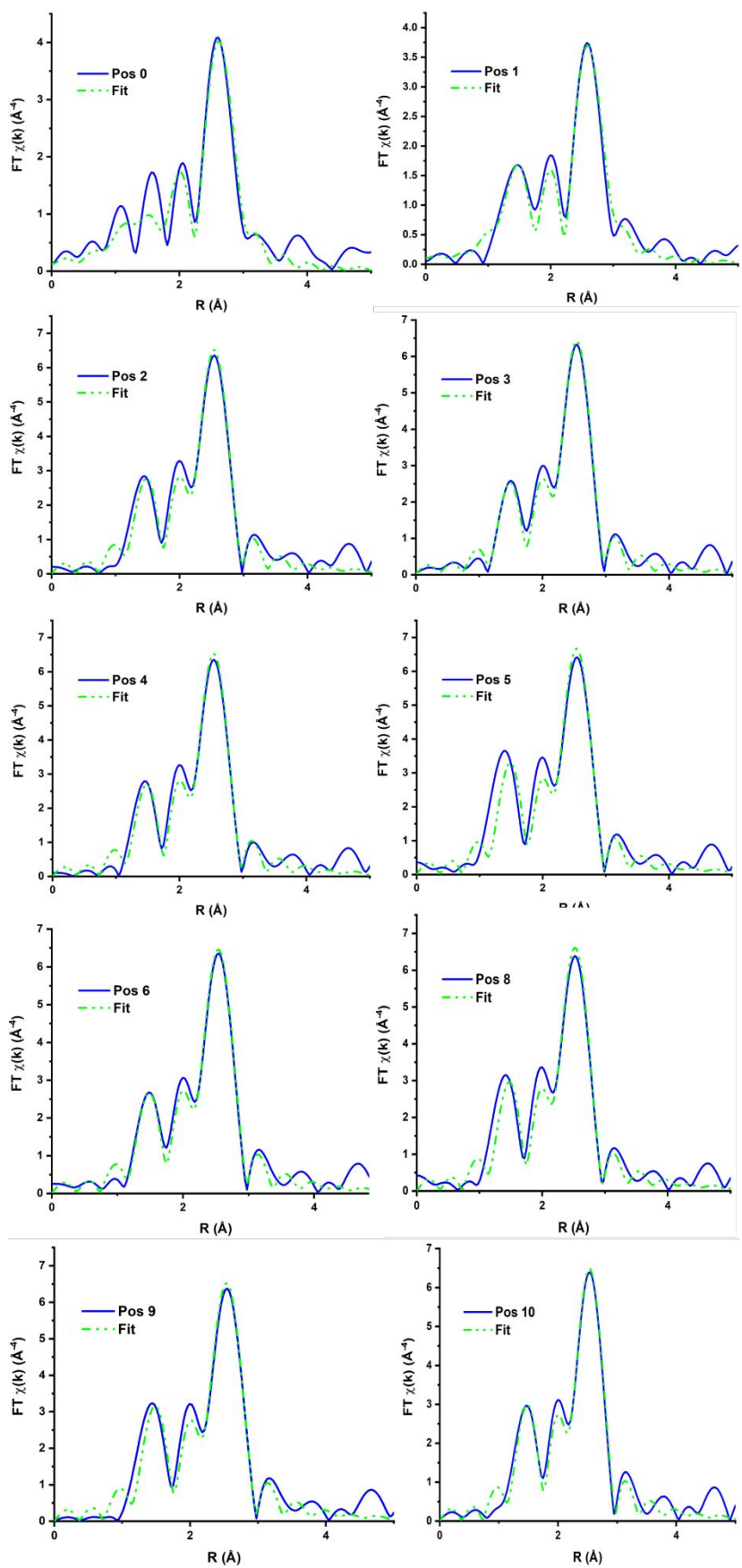
**Figure S3.** EXAFS Fit (R space top, k-space bottom) of Pd/Al<sub>2</sub>O<sub>3</sub> at 100 °C under reaction conditions, at various position along the bed

**Table S2.** XAFS Fit results for Pd/Al<sub>2</sub>O<sub>3</sub> at 100 °C under reaction conditions, at various position along the bed

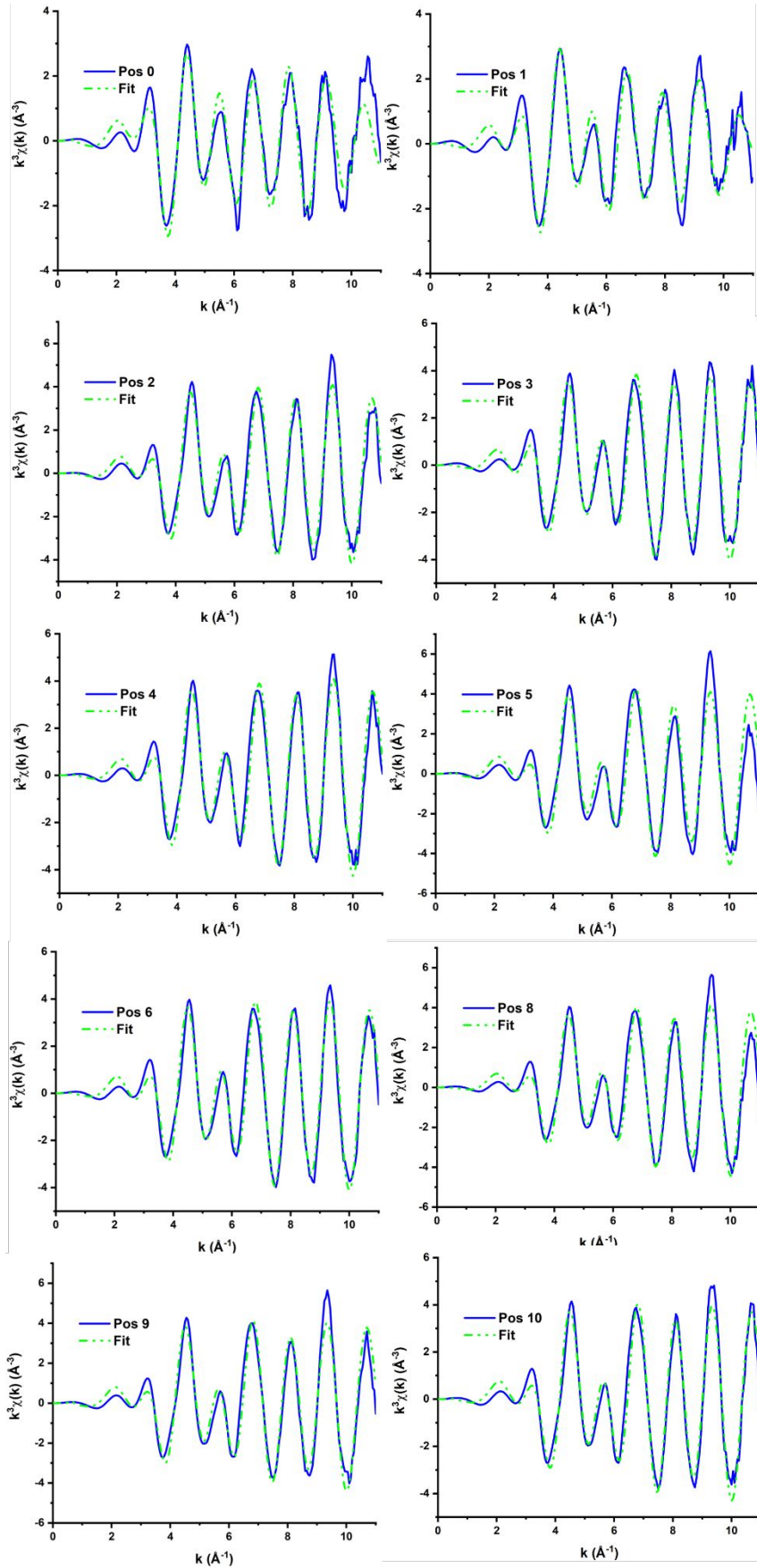
Position	CN <sub>Pd-Pd</sub>	R <sub>Pd-Pd</sub> (Å)	σ <sub>Pd-Pd</sub>	CN <sub>Pd-N/O</sub>	R <sub>Pd-N/O</sub> (Å)	σ <sub>Pd-N/O</sub>	ΔE	R <sub>factor</sub>
0	9.3 ± 1.6	2.82 ± 0.01	0.014 ± 0.002	2.2 ± 0.6	1.97 ± 0.02	0.007 ± 0.005	1.16 ± 1	0.0415235
1	8.7 ± 1.1	2.83 ± 0.01	0.015 ± 0.002	3.5 ± 1.1	1.96 ± 0.02	0.014 ± 0.006	2.4 ± 0.8	0.0209122
2	7.4 ± 1.3	2.83 ± 0.01	0.015 ± 0.002	1.9 ± 0.8	1.97 ± 0.02	0.009 ± 0.007	0.8 ± 0.9	0.0254434
3	9.7 ± 1.4	2.83 ± 0.01	0.015 ± 0.002	1.7 ± 0.7	1.96 ± 0.02	0.007 ± 0.006	2.5 ± 0.9	0.0245970
4	9.3 ± 1.3	2.83 ± 0.01	0.015 ± 0.002	1.9 ± 0.7	1.98 ± 0.02	0.007 ± 0.005	1.7 ± 0.9	0.0225474
5	9.4 ± 1.5	2.83 ± 0.01	0.015 ± 0.002	1.8 ± 0.6	1.98 ± 0.02	0.005 ± 0.004	2 ± 1	0.0343935
6	9.7 ± 1.3	2.83 ± 0.01	0.015 ± 0.002	1.8 ± 0.5	2 ± 0.013	0.003 ± 0.002	1.1 ± 0.9	0.0204712
8	9.6 ± 1.2	2.83 ± 0.01	0.015 ± 0.002	2.1 ± 0.8	1.96 ± 0.02	0.01 ± 0.007	2.6 ± 0.8	0.0211301
9	9.5 ± 1.4	2.83 ± 0.01	0.015 ± 0.002	1.7 ± 0.7	1.97 ± 0.02	0.007 ± 0.006	2.9 ± 1	0.0279799
10	9.5 ± 1.2	2.83 ± 0.01	0.015 ± 0.002	1.6 ± 0.6	1.97 ± 0.02	0.006 ± 0.005	1.5 ± 0.8	0.0203464

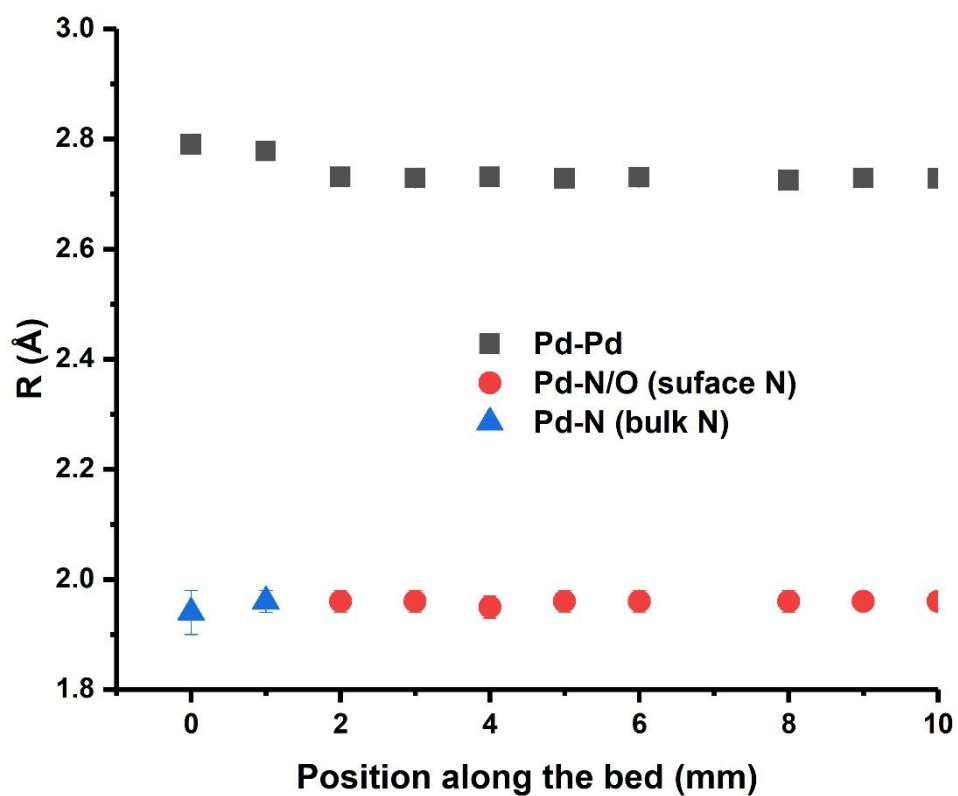


**Figure S4** Components obtained from MCR (left), reference Pd spectra for PdO, Pd<sup>0</sup> and PdN<sub>x</sub> (right)



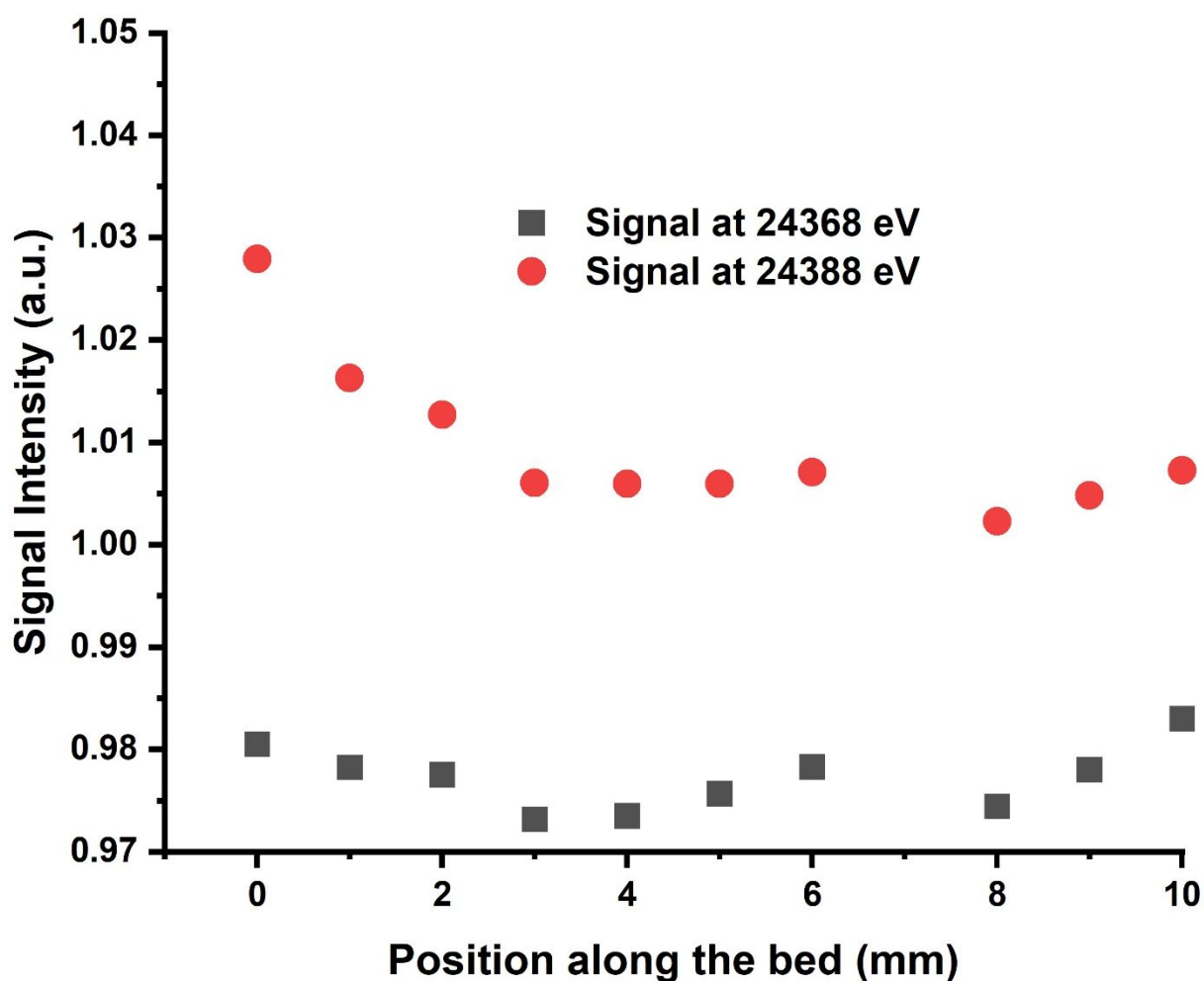






**Figure S5.** EXAFS Fit (R space top, k-space middle) of Pd/Al<sub>2</sub>O<sub>3</sub> at 175 °C under reaction conditions, at various position along the bed. At the bottom Pd-Pd and Pd-N/O distances obtained from EXAFS fit (the error is present but smaller than the symbol size).



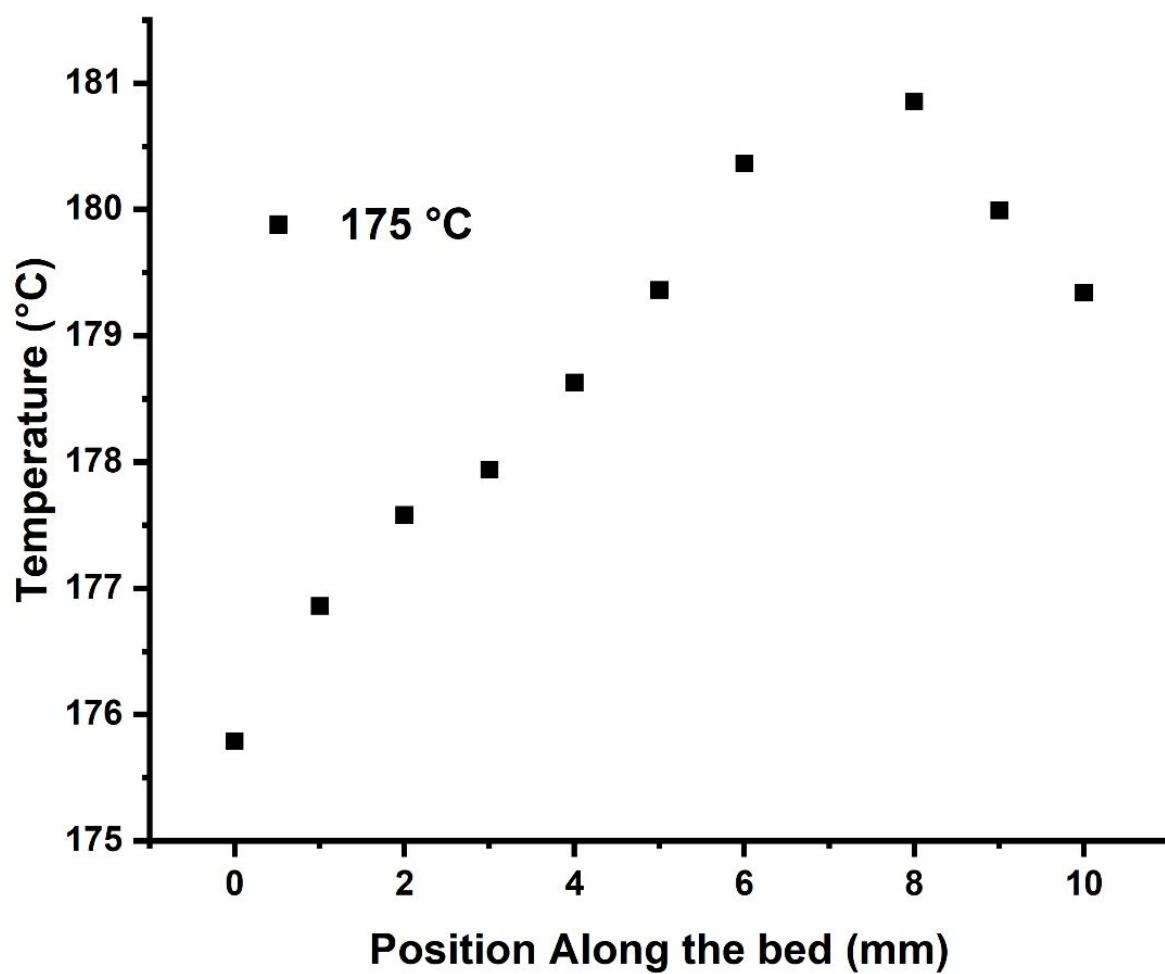


**Figure S6.** Intensity of XANES at the whiteline (24368 eV) and at the PdN<sub>x</sub> peak (24388 eV) along the catalyst bed for Pd/Al<sub>2</sub>O<sub>3</sub> at 175 °C

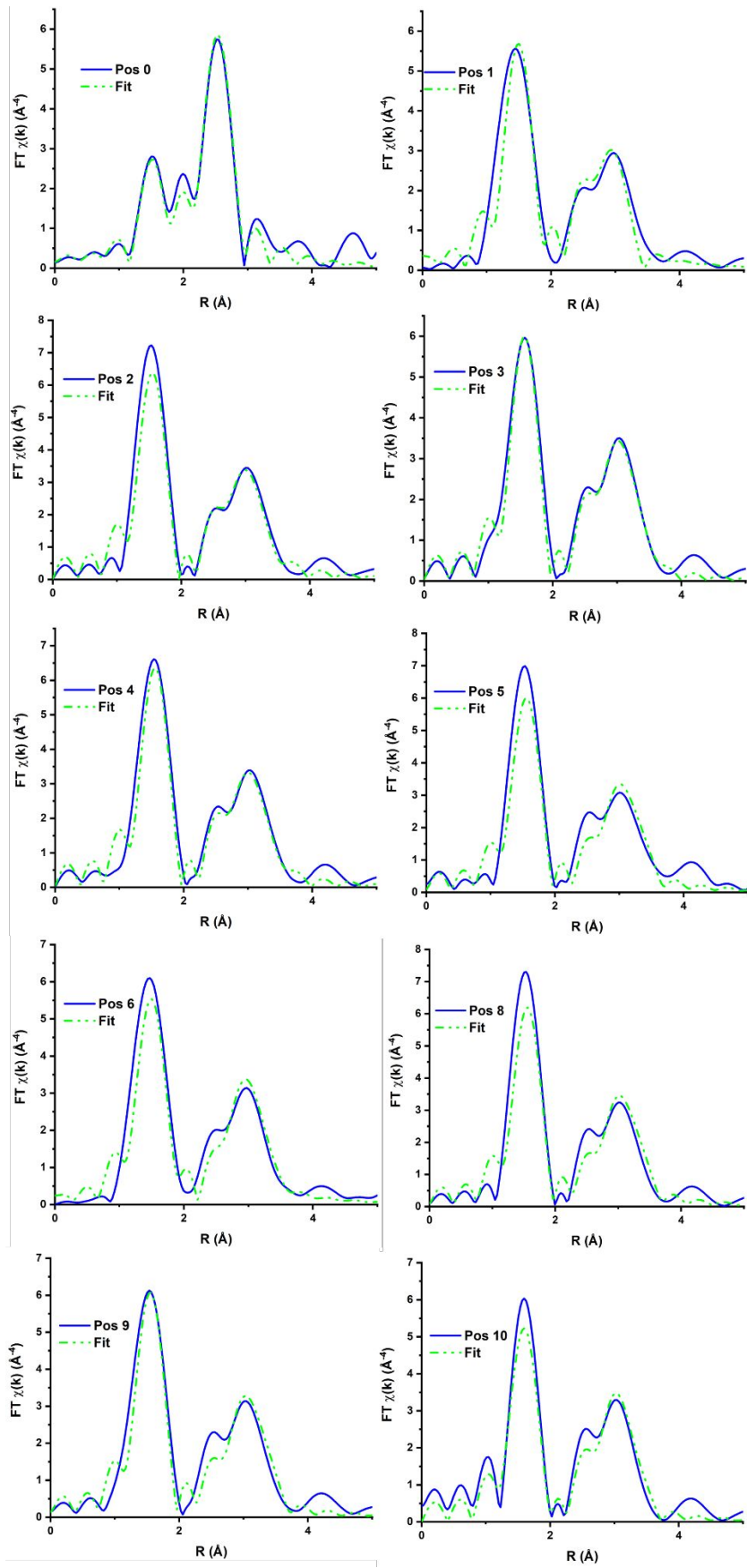
**Table S3.** XAFS Fit results for Pd/Al<sub>2</sub>O<sub>3</sub> at 175 °C under reaction conditions, at various position along the bed

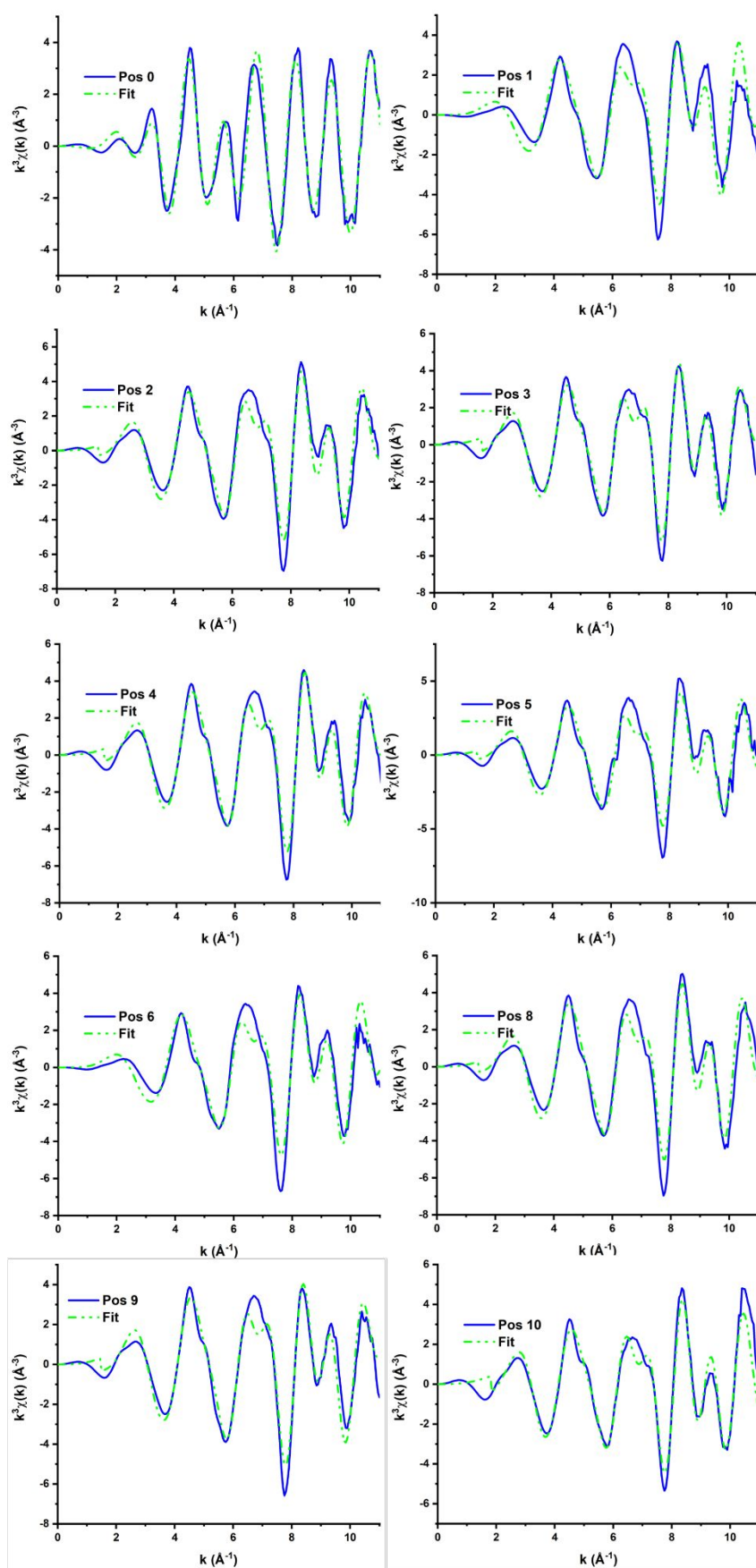
Position	CN <sub>Pd-Pd</sub>	R <sub>Pd-Pd</sub> (Å)	σ <sub>Pd-Pd</sub>	CN <sub>Pd-N/O</sub>	R <sub>Pd-N/O</sub> (Å)	σ <sub>Pd-N/O</sub>	ΔE	R <sub>factor</sub>
0	9.4 ± 1.3	2.79 ± 0.01	0.015 ± 0.002	2.3 ± 2.3	1.94 ± 0.04	0.02 ± 0.02	1.16 ± 1	0.0286633
1	9.5 ± 1.3	2.78 ± 0.01	0.017 ± 0.002	1.2 ± 0.6	1.96 ± 0.02	0.005 ± 0.007	1.4 ± 0.9	0.0243842
2	7.6 ± 0.8	2.731 ± 0.008	0.01 ± 0.001	1.37 ± 0.4	1.96 ± 0.02	0.004 ± 0.004	1 ± 0.9	0.0167424
3	8 ± 0.8	2.729 ± 0.008	0.011 ± 0.001	0.95 ± 0.4	1.96 ± 0.02	0.002 ± 0.004	1.7 ± 0.8	0.0139241
4	7.7 ± 0.8	2.731 ± 0.007	0.01 ± 0.001	1 ± 0.4	1.95 ± 0.02	0.002 ± 0.004	1.7 ± 0.9	0.0150922
5	7.2 ± 1.2	2.73 ± 0.01	0.01 ± 0.001	1.5 ± 0.6	1.96 ± 0.02	0.003 ± 0.005	2 ± 1	0.0143951
6	7.7 ± 0.8	2.73 ± 0.008	0.01 ± 0.001	1.2 ± 0.4	1.96 ± 0.02	0.003 ± 0.004	1.5 ± 0.8	0.0270971

8	$7.3 \pm 1$	$2.725 \pm 0.009$	$0.01 \pm 0.001$	$1.3 \pm 0.5$	$1.96 \pm 0.02$	$0.003 \pm 0.05$	$0.5 \pm 1$	0.0281644
9	$7.4 \pm 0.8$	$2.729 \pm 0.009$	$0.01 \pm 0.001$	$1.4 \pm 0.4$	$1.96 \pm 0.01$	$0.003 \pm 0.004$	$1.9 \pm 1$	0.0215773
10	$7.4 \pm 0.8$	$2.728 \pm 0.007$	$0.01 \pm 0.001$	$1.4 \pm 0.4$	$1.96 \pm 0.01$	$0.003 \pm 0.004$	$1.4 \pm 0.8$	0.0146797

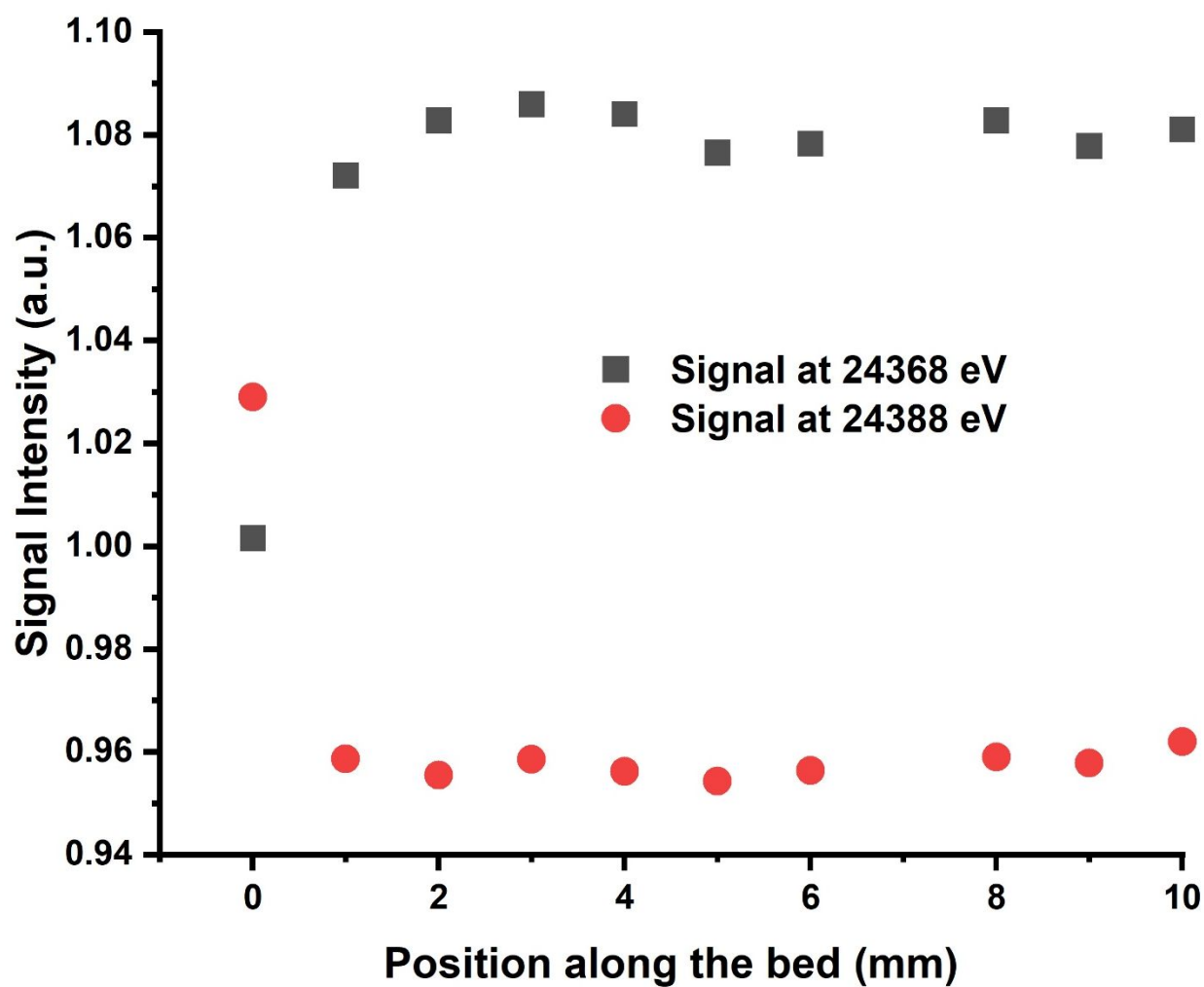


**Figure S7.** Temperature recorded at various position along the bed during reaction conditions.





**Figure S8.** EXAFS Fit (R space top, k-space bottom) of Pd/Al<sub>2</sub>O<sub>3</sub> at 300 °C under reaction conditions, at various position along the bed

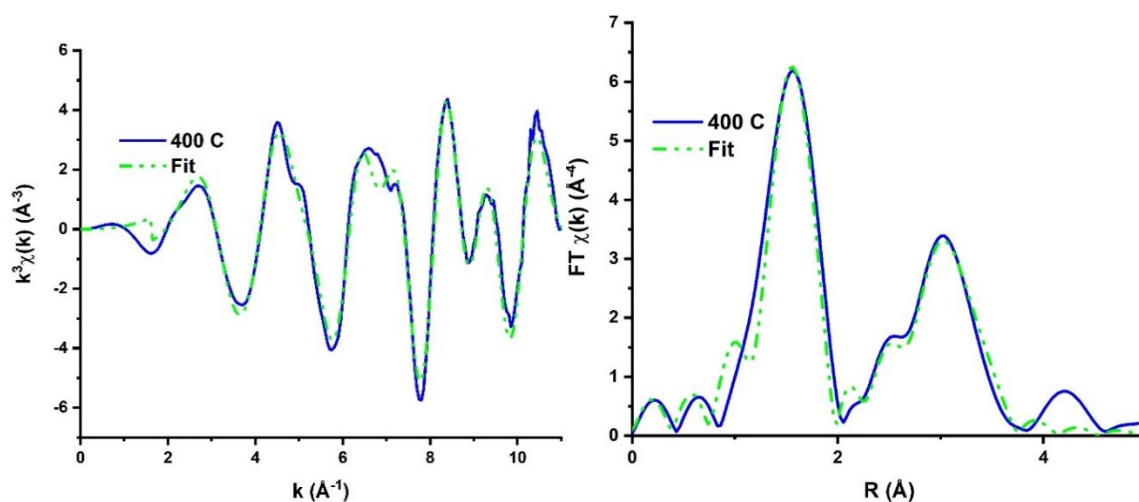


**Figure S9.** Intensity of XANES at the whiteline (24368 eV) and at the PdN<sub>x</sub> peak (24388 eV) along the catalyst bed for Pd/Al<sub>2</sub>O<sub>3</sub> at 300 °C

**Table S4.** XAFS Fit results for Pd/Al<sub>2</sub>O<sub>3</sub> at 300 °C under reaction conditions, at various position along the bed. For the position 1-10 the Debye-Waller for all path was fixed to 0.03 due to the high correlation with the coordination number and to reduce the number of independent parameter.

Position	CN <sub>Pd-Pd</sub>	R <sub>Pd-Pd</sub> (Å)	σ <sub>Pd-Pd</sub>	CN <sub>Pd-N/O</sub>	R <sub>Pd-N/O</sub> (Å)	σ <sub>Pd-N/O</sub>	ΔE	R <sub>factor</sub>
0	8.1 ± 0.9	2.72 ± 0.01	0.012 ± 0.001	0.8 ± 0.3	1.98 ± 0.02	0.002 ± 0.003	0.4 ± 0.9	0.0155870
Position	CN <sub>Pd-O</sub>	R <sub>Pd-O</sub> (Å)	CN <sub>Pd-Pd1</sub> <sup>*</sup>	R <sub>Pd-Pd1</sub> <sup>*</sup> (Å)	CN <sub>Pd-Pd2</sub> <sup>*</sup>	R <sub>Pd-Pd2</sub> <sup>*</sup> (Å)	ΔE	R <sub>factor</sub>
1	3.7 ± 0.6	2.02 ± 0.03	1.3 ± 0.7	3.05 ± 0.03	2 ± 1	3.41 ± 0.04	-5 ± 4	0.0762870
2	3.7 ± 0.4	2.04 ± 0.02	1.7 ± 0.7	3.06 ± 0.03	2.2 ± 1	3.44 ± 0.03	7 ± 2	0.0480747
3	3.4 ± 0.3	2.04 ± 0.02	1.8 ± 0.5	3.07 ± 0.03	2.3 ± 0.6	3.46 ± 0.02	10 ± 1	0.0184511
4	3.6 ± 0.4	2.03 ± 0.02	1.6 ± 0.6	3.06 ± 0.02	2.3 ± 0.8	3.45 ± 0.02	9 ± 2	0.0322944
5	3.5 ± 0.4	2.03 ± 0.02	1.5 ± 0.7	3.06 ± 0.03	2 ± 1	3.43 ± 0.03	8 ± 2	0.0551810
6	3.7 ± 0.6	2.02 ± 0.02	1.4 ± 0.7	3.04 ± 0.03	2.4 ± 1	3.41 ± 0.04	-5 ± 4	0.0628919
8	3.6 ± 0.4	2.03 ± 0.03	1.6 ± 0.7	3.06 ± 0.03	2.2 ± 1	3.44 ± 0.03	8 ± 2	0.0571194
9	3.5 ± 0.4	2.03 ± 0.02	1.4 ± 0.6	3.06 ± 0.03	2.3 ± 0.7	3.45 ± 0.02	8.5 ± 2	0.0355347
10	2.9 ± 0.3	2.05 ± 0.03	1.9 ± 0.4	3.08 ± 0.02	1.6 ± 0.6	3.47 ± 0.02	13 ± 1	0.0229180

\*The scattering path for these fits were obtained from a PdO reference file.



**Figure S10.** EXAFS (k-space on the left, R space on the right) Fit of Pd/Al<sub>2</sub>O<sub>3</sub> at 400 °C under reaction conditions.

**Table S5.** XAFS Fit results for Pd/Al<sub>2</sub>O<sub>3</sub> at 400 °C under reaction conditions. The Debye-Waller for all path was fixed to 0.03 due to the high correlation with the coordination number and to reduce the number of independent parameter.

CN <sub>Pd-O</sub>	R <sub>Pd-O</sub> (Å)	CN <sub>Pd-PdO1</sub>	R <sub>Pd-PdO1</sub> (Å)	CN <sub>Pd-PdO2</sub>	R <sub>Pd-PdO2</sub> (Å)	ΔE	R <sub>factor</sub>
3.8 ± 0.2	2.02 ± 0.01	1.4 ± 0.4	3.02 ± 0.02	2.2 ± 0.6	3.45 ± 0.02	8.5 ± 1	0.0202641