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SUPPLEMENTARY INFORMATION

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Structural selectivity of supported Pd nanoparticles for catalytic NH_3 oxidation resolved using combined operando spectroscopy

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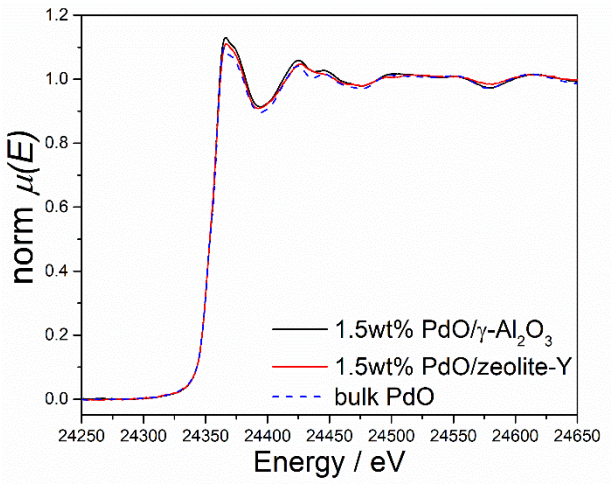
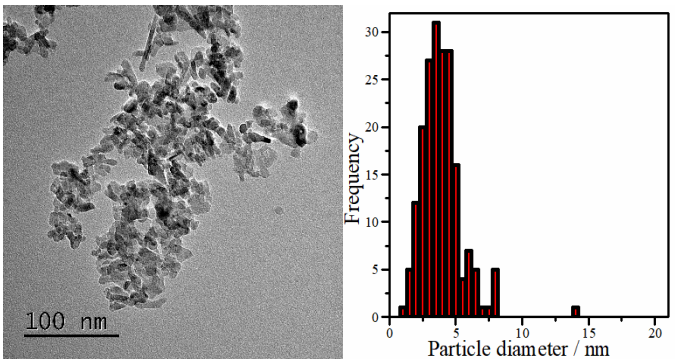
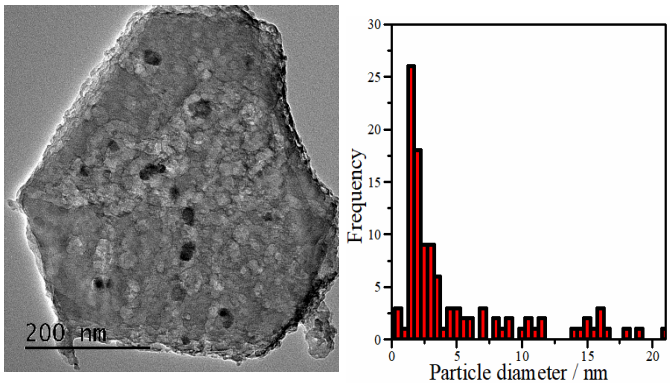
Supplementary Information



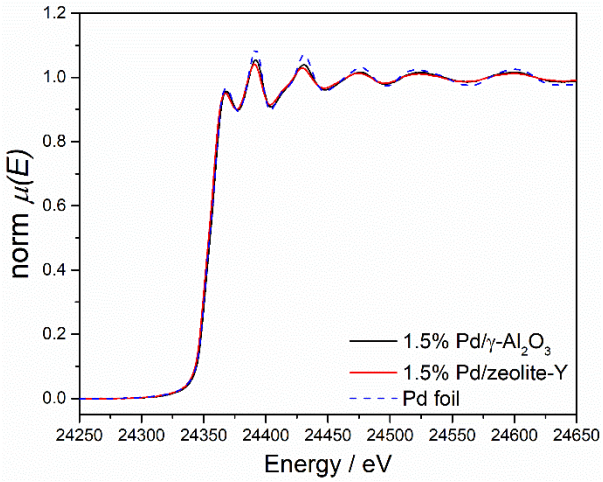
Supplementary Figure 1. *Pd K-edge XANES of calcined catalysts PdO/γ-Al_2O_3 (black) and PdO/zeolite-Y (red) before catalyst testing and a reference Pd K-edge XANES of bulk PdO (blue, dashed).*



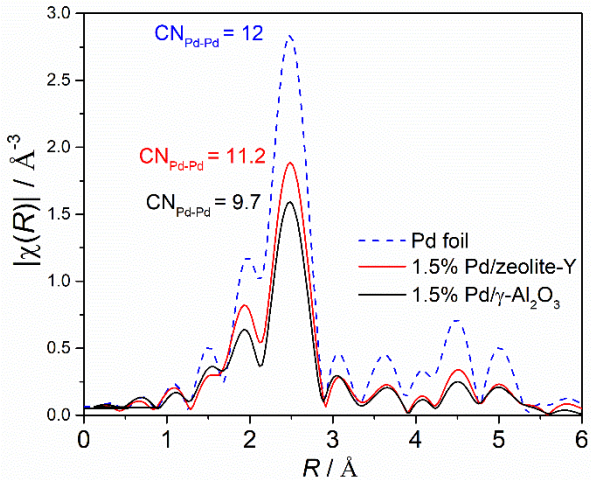
Supplementary Figure 2. *TEM images and corresponding histogram of particle size distribution of PdO/γ-Al_2O_3*



Supplementary Figure 3. *TEM images and corresponding histogram of particle size distribution of PdO/zeolite-HY*



Supplementary Figure 4. *Pd K-edge XANES of reduced catalysts Pd/γ-Al_2O_3 (black) and Pd/zeolite-Y (red) at 100°C after pre-treatment in H_2, and a reference spectrum of Pd foil (blue, dashed).*

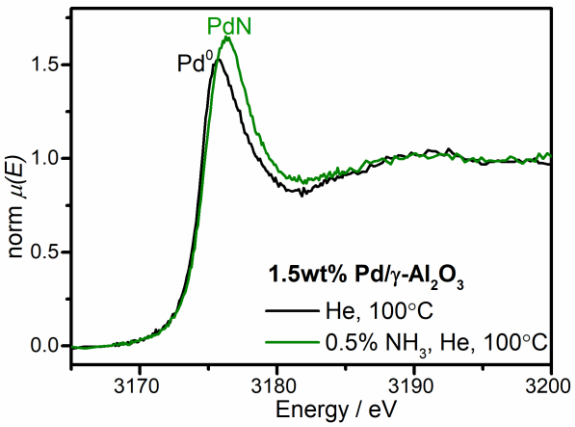


Supplementary Figure 5. *Non phase corrected Fourier transformed Pd K-edge EXAFS of supported Pd catalysts after reduction pre-treatment; Pd/γ-Al_2O_3 (black), Pd/zeolite-Y (red) and Pd foil reference (blue, dashed). Annotated with corresponding Pd-Pd coordination numbers, $R_{Pd\text{-}Pd}$ = 2.734 Å.*

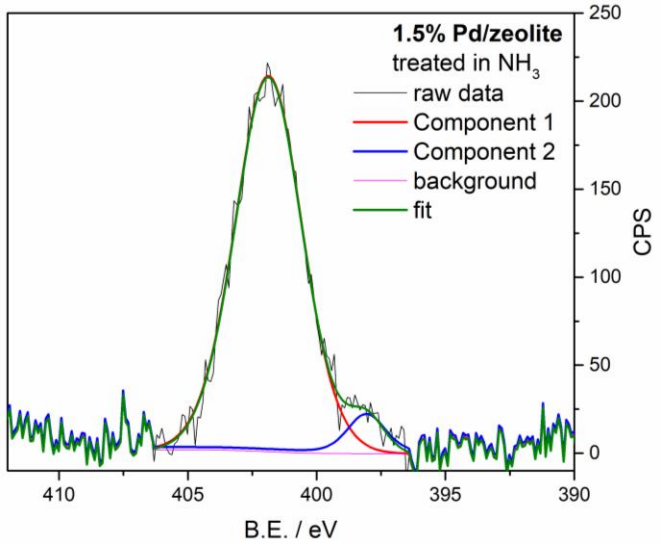
Supplementary Table 1. *EXAFS fitting parameters of supported Pd catalysts after reduction pre-treatment.*

		N	***R* / Å**	**σ^2 / Å²**	**E_0 / eV**	***R* factor**
Pd/γ-Al_2O_3	Pd-Pd	9.7 (4)	2.734(3)	0.008	(-)6.1(5)	0.02
Pd/zeolite-Y	Pd-Pd	11 (1)	2.734(3)	0.0082(7)	(-)5.2(4)	0.03
Pd foil	Pd-Pd	12	2.734	0.0052(3)	(-)6.0(2)	0.005

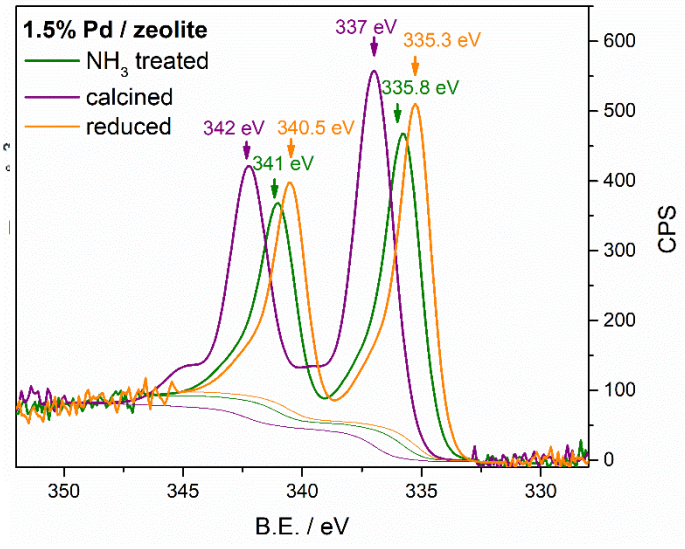
Note: Fitting parameters S_0^2 = 0.8; Fit range 3 < *k* / Å^{-2} < 14, 1 < *R* / Å < 3; Number of independent points = 14.



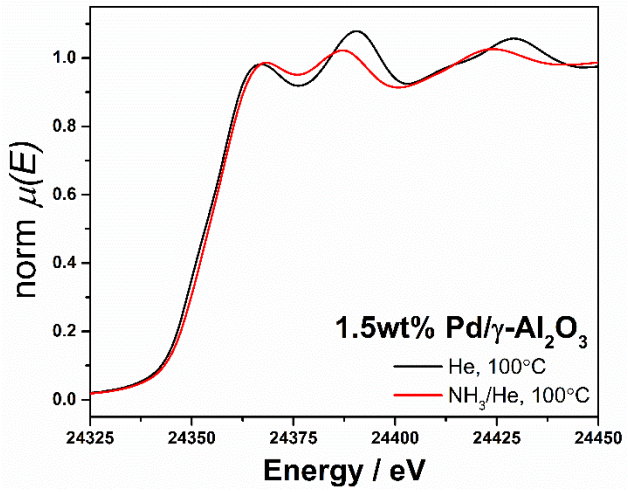
Supplementary Figure 6*. Pd L_3-edge XANES of Pd/γ-Al_2O_3 after a reduction pre-treatment in H_2, then exposure to a) He (black) and b) 0.5% NH_3/He at 100°C (green).*



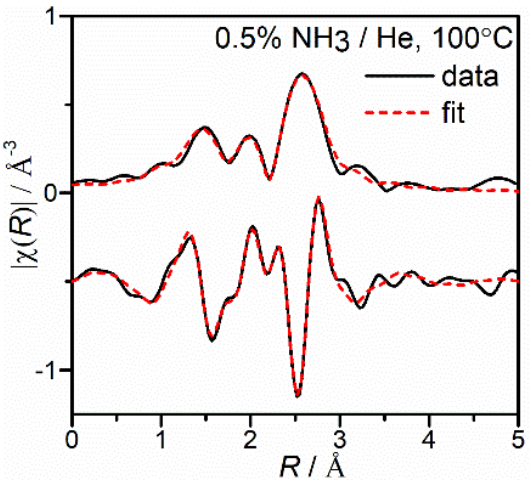
Supplementary Figure 7. *N1s XPS spectrum of Pd/zeolite-Y sample after treatment in 0.5% NH_3/He at 100°C.*



Supplementary Figure 8. *Pd 3d XPS spectrum of Pd/zeolite-Y sample after treatment in a) air, 500°C (purple) b) 10%H_2/He, 200°C (orange), and c) 0.5% NH_3/He at 100°C (green).*



Supplementary Figure 9. *Pd K-edge XANES of Pd/γ-Al_2O_3 catalyst before and after switching to NH_3/He gas feed.*



Supplementary Figure 10. *Magnitude (top) and imaginary (bottom) parts of Fourier transformed Pd K-edge EXAFS of Pd/γ-Al_2O_3 at 100°C under 0.5% NH_3/ He (black) and the plotted fitting model (red, dashed).*

Supplementary Table 2. Pd K-edge EXAFS fitting parameters of 1.5wt% Pd/γ-Al_2O_3 at 100°C in 0.5% NH_3/He.

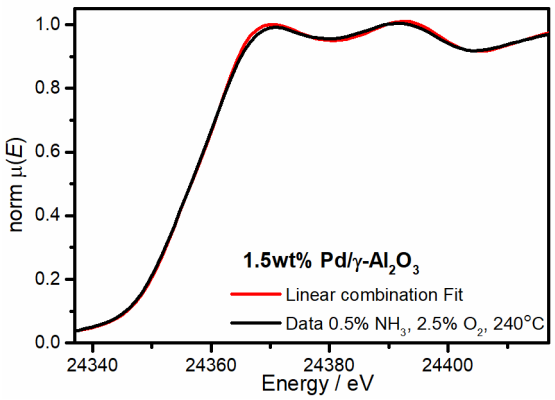
Abs - Scat	*N*	*R* / Å	σ^2 / Å^2	E_0 / eV	R_{factor}
Pd-N	1.0(4)	1.99(2)	0.001(5)	-4.5(9)	0.009
Pd-Pd	9(1)	2.81(1)	0.016(2)		

Note: Fitting parameters S_0^2 = 0.8; Fit range 3 < *k* / Å^{-2} < 10.6, 1 < *R* / Å < 3; Number of independent points = 9.

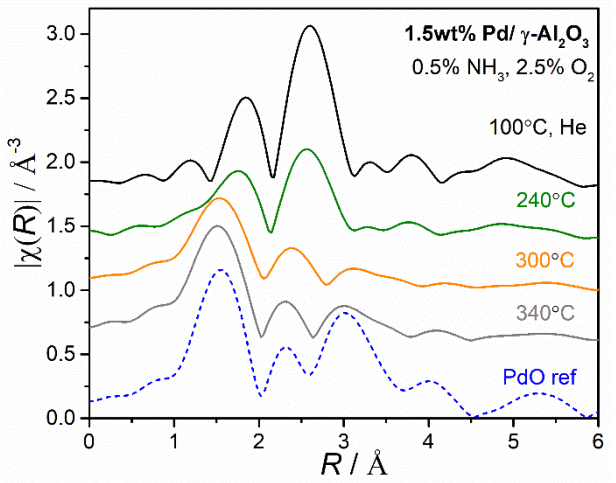
Supplementary Table 3*.Linear Combination Fitting analysis of Pd/γ-Al_2O_3 Pd K-edge XANES at 240°C during NH_3 oxidation conditions (0.5% NH_3/ 2.5% O_2/ He).*

Data	Pd/γ-Al_2O_3, 100°C, He	Pd/γ-Al_2O_3, 300°C, NH_3/O_2/He	R_{factor}
Pd/γ-Al_2O_3, 240°C, NH_3/O_2/He	0.60(1)	0.40(1)	0.0003

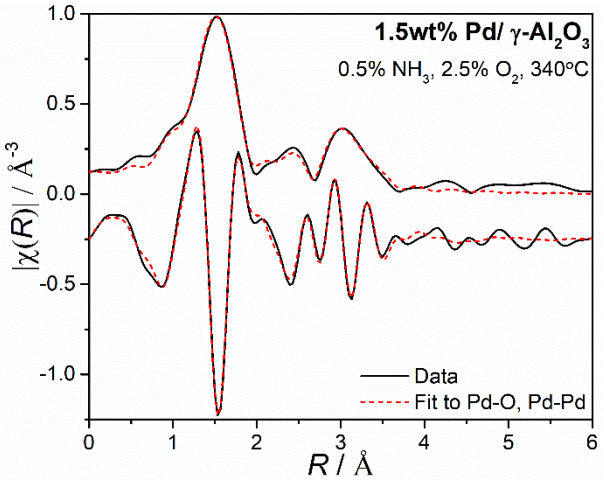
Note: Fitting parameters. Fit range 24333 ≤ *E* / eV ≤ 24403; Number of data points = 65. Weights sum to 1



Supplementary Figure 11. *Pd K-edge XANES of Pd/γ-Al_2O_3 at 240°C in 0.5% NH_3/ 2.5% O_2/ He (black) and a model fitted from linear combination analysis between 24333 to 24403 eV (red).*



Supplementary Figure 12. *Fourier transformed Pd K-edge EXAFS of Pd/γ-Al_2O_3 at increasing temperatures under 0.5% NH_3/ 2.5% O_2/ He. Plotted with Fourier transformed Pd K-edge EXAFS of Pd/γ-Al_2O_3 under inert atmosphere (He) at 100°C (black) and a bulk PdO reference collected at room temperature (blue, dashed).*

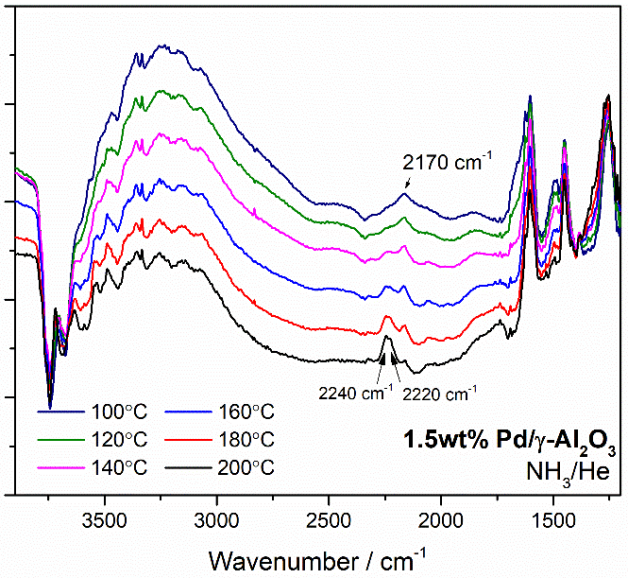


Supplementary Figure 13*. Magnitude (top) and imaginary (bottom) parts of Fourier transformed Pd K-edge EXAFS of Pd/γ-Al_2O_3 at 340°C under 0.5% NH_3/ 2.5% O_2/ He (black) and the plotted fitting model (red, dashed).*

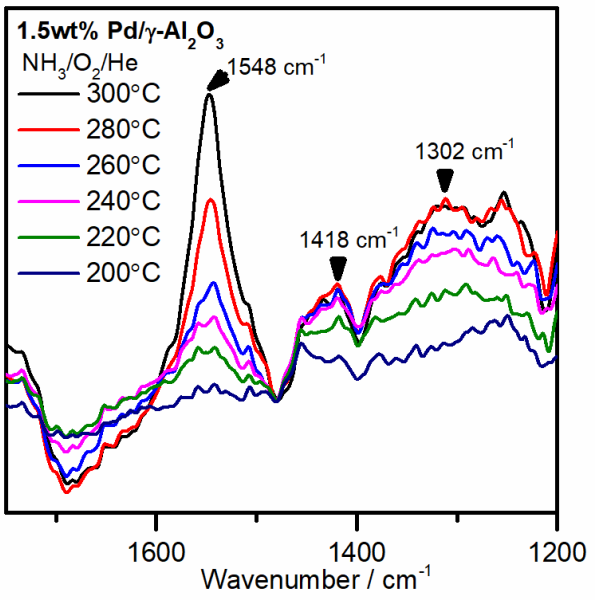
Supplementary Table 4. *Pd K-edge EXAFS fitting parameters of Pd/γ-Al_2O_3 at 340°C in 0.5% NH_3/2.5% O_2/ He gas flow.*

Abs - Scat	**N**	**R / Å**	**σ^2 / Å^2**	**E_0 / eV**	**R_{factor}**
Pd-O	3.7(3)	2.01(1)	0.004(1)	6(1)	0.005
Pd-Pd$_{(1)}$	1.0(9)	3.01(1)	0.003(1)		
Pd-Pd$_{(2)}$	2(2)	3.455(5)	0.004(8)		

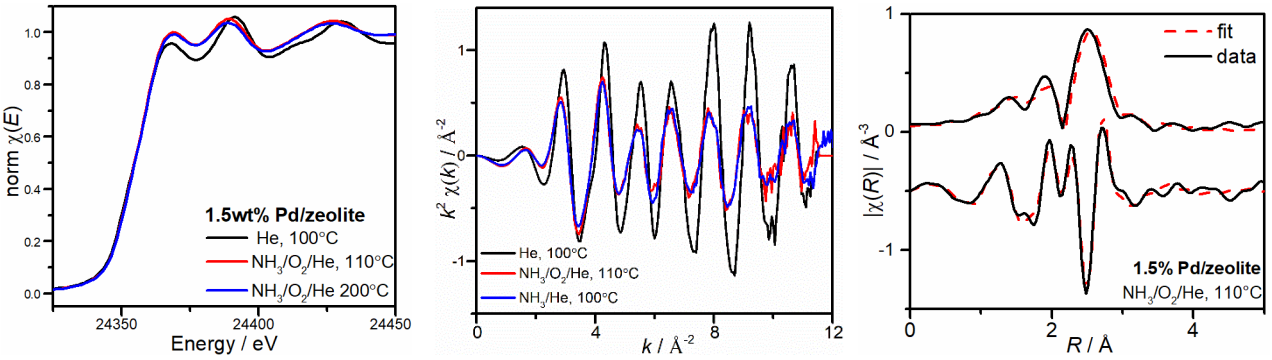
Note: Fitting parameters S_0^2 = 0.8; Fit range 3 < *k* / Å^{-2} < 10.6, 1 < *R* / Å < 3; Number of independent points = 14.



Supplementary Figure 14. *Difference DRIFTS spectrum of 1.5wt% Pd/γ-Al_2O_3 after reduction pre-treatment in He then switching to 0.5% NH_3 /He gas feed at increasing temperatures (100°C to 200°C).*



Supplementary Figure 15*. Difference DRIFTS spectra of Pd/γ-Al_2O_3 after switching from He to 0.5% NH_3/2.5% O_2/He at increasing temperatures.*

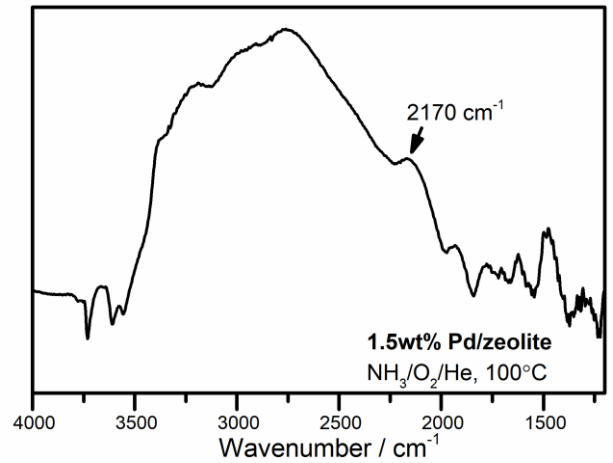


Supplementary Figure 16. *Pd K-edge XANES of 1.5wt% Pd/zeolite after reduction pre-treatment in H_2, then exposure to a) He at 100°C (black), b) 0.5% NH_3/2.5% O_2/He at 110°C (red) and c) 0.5% NH_3/2.5% O_2/He at 200°C (blue).* ***Supplementary Figure 17.****. Pd K-edge k^2 weighted EXAFS of 1.5wt% Pd/zeolite after reduction pre-treatment, then exposure to a) He (black) and b) 0.5%NH_3/2.5% O_2/He (red) and c) 0.5% NH_3/He (blue) at 100°C.* ***Supplementary Figure 18.*** *Stacked plot of magnitude (top) and imaginary (bottoms) non-phase corrected Fourier transformed Pd K-edge EXAFS of 1.5wt% Pd/zeolite at 100°C in 0.5% NH_3/2.5% O_2/He atmosphere, plotted with fit constructed from Pd-N and Pd-Pd scattering paths.*

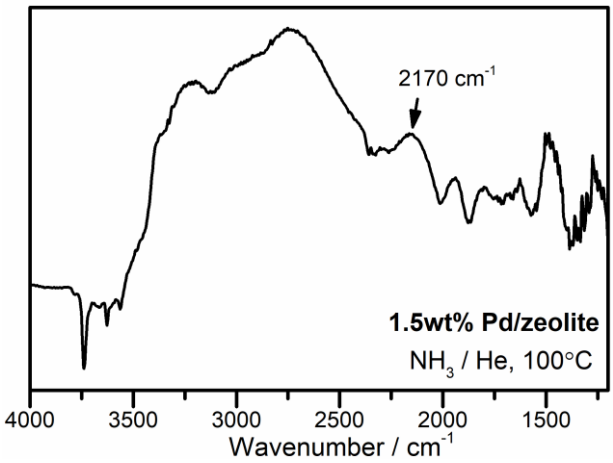
Supplementary Table 4. *Pd K-edge EXAFS fitting parameters of 1.5wt% Pd/zeolite at 110°C in 0.5% NH_3/2.5%O_2/He.*

Abs - Scat	***N***	***R* / Å**	**σ^2 / Å²**	**E_0 / eV**	**R_{factor}**
Pd-N	1.6(4)	1.99(3)	0.014(5)	-4.2(6)	0.04
Pd-Pd	9.1(5)	2.780(5)	0.0126(7)		

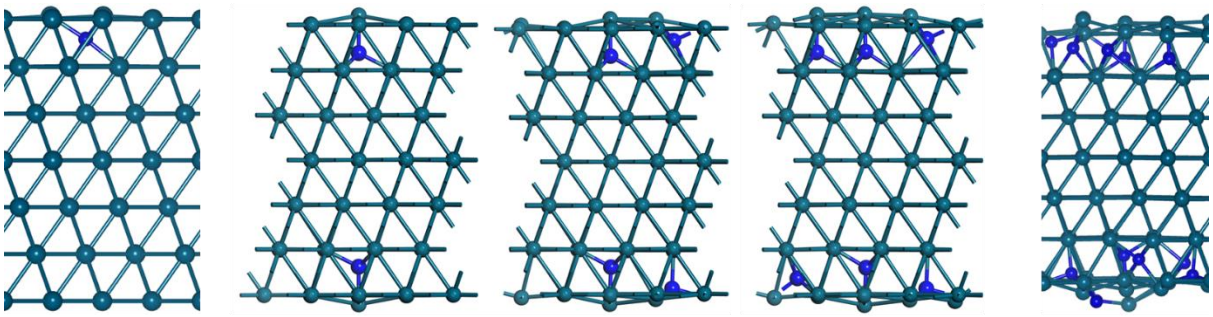
Note: Fitting parameters S_0^2 = 0.8; Fit range 3 < *k* / Å^{-2} < 10.6, 1.1 < *R* / Å < 3; Number of independent points = 12.



***Supplementary Figure 19**. Difference DRIFTS spectrum of Pd/zeolite after switching from He to 0.5% NH_3/ 2.5% O_2/ He at 100°C.*

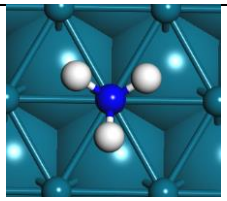
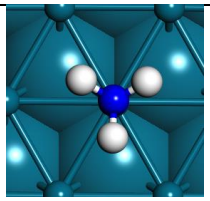


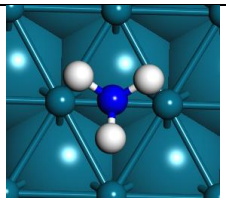
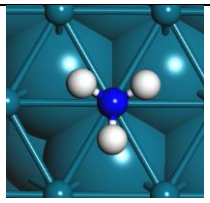
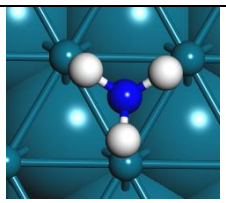
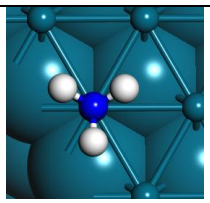
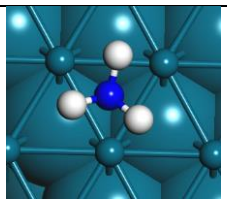
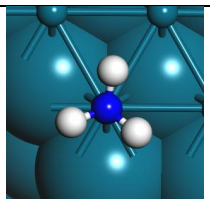
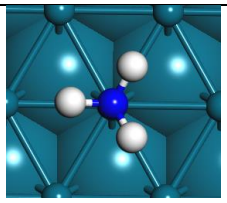
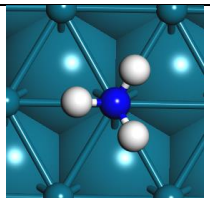
***Supplementary Figure 20.** Difference DRIFTS spectrum of Pd/zeolite after switching from He to 0.5% NH_3/ He at 100°C.*



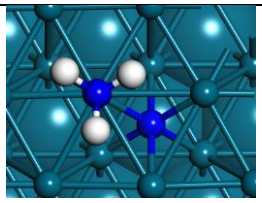
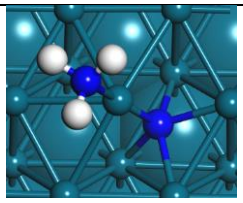
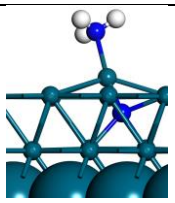
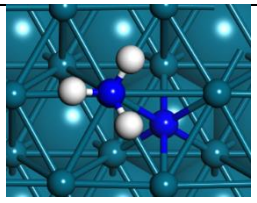
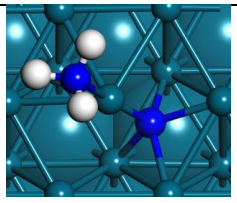
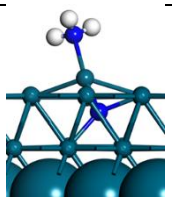
***Supplementary Figure 21**. The optimised structures for the Pd(111) system with 0.12 wt%, 0.23 wt%, 0.47 wt%, 0.70 wt%, and 1.39 wt% of interstitial N-atoms, which correspond to the number of interstitial N-atoms used being 1, 2, 4, 6, and 12, respectively. For all these calculations we placed the N-atoms at centre of the octahedral sites that are close to both the exposed surfaces and relaxed the atomic coordinates within a fixed cell. In the system with 0.12 wt%, the interstitial N-atom was placed only in one of the two exposed surfaces and as there is only one N-atom. Of the seven atomic layers, the bottom four layers were fixed but the upper three layers along with the interstitial N-atom were allowed to relax.*

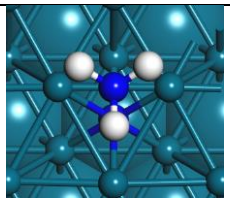
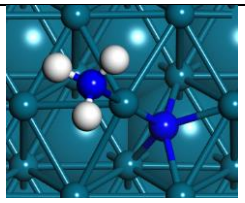
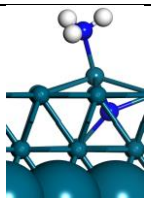
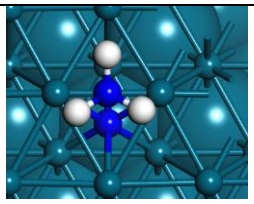
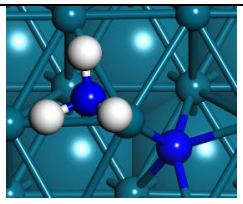
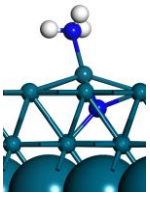
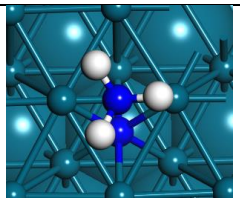
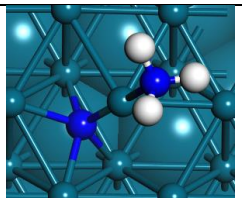
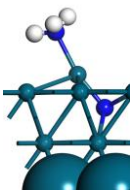
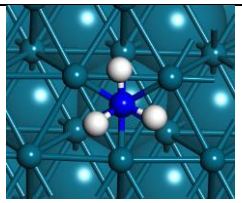
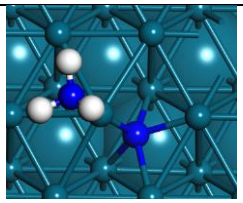
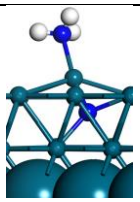
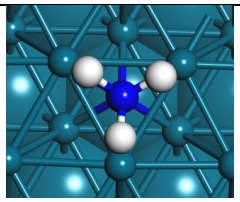
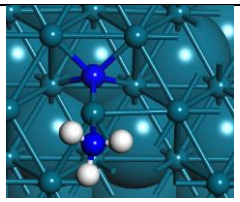
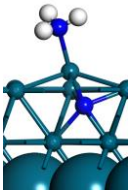
***Supplementary Table 6.** Calculated adsorption energies of an NH_3 molecule adsorbed on pristine Pd(111) surface in multiple configurations, showing initial configuration, relaxed configuration and the associated adsorption energy. Atomic coordination values of the reported computational models are provided in the data repository (DOI 10.5258/SOTON/D0709).*

Initial configuration		**Relaxed Configuration**		**E_{ad} / eV**
$(NH_3)_{top}$ (N_{top}- H_{HCP})		**$(NH_3)_{top}$ (N_{top}- H_{HCP})**		**-1.033**

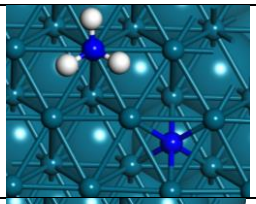
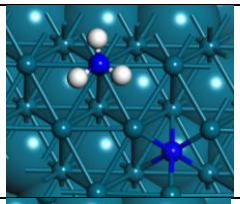
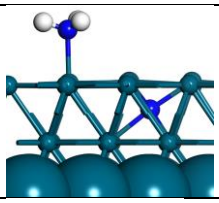
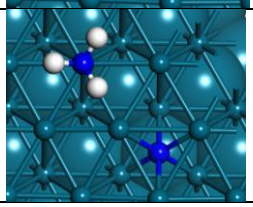
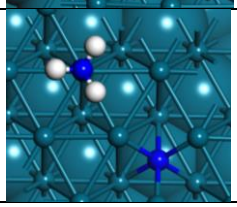
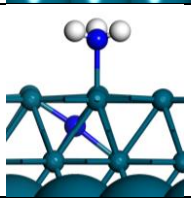
$(NH_3)_{bdg}$		$(NH_3)_{top}$ $(N_{top}$- $H_{HCP})$		-1.032
$(NH_3)_{hcp}$ $(N_{hcp}$- $H_{top})$		$(NH_3)_{top}$ $(N_{top}$- $H_{HCP})$		-1.032
$(NH_3)_{hcp}$ $(N_{hcp}$- $H_{bdg})$		$(NH_3)_{top}$ $(N_{top}$- $H_{HCP})$		-1.031
$(NH_3)_{top}$ $(N_{top}$- $H_{bdg})$		$(NH_3)_{top}$ $(N_{top}$- $H_{bdg})$		-1.031

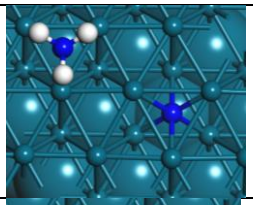
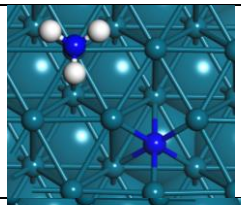
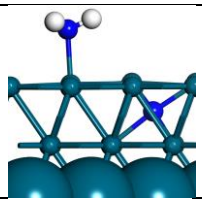
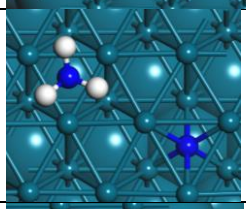
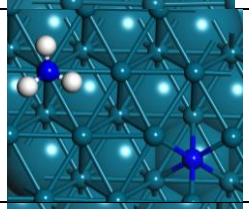
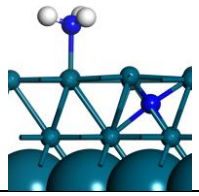
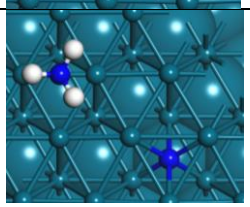
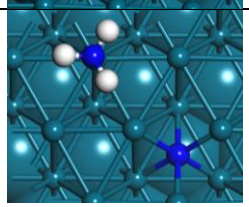
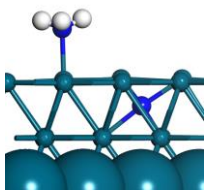
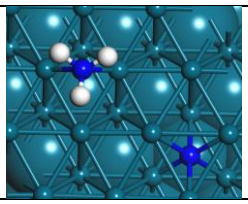
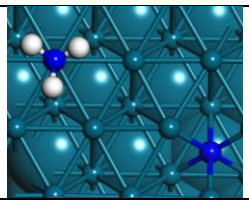
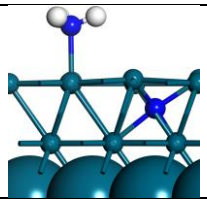
Supplementary Table 7. *Calculated adsorption energies of an NH_3 molecule adsorbed on Pd(111) surface near an interstitial N-atom site in multiple configurations, showing initial configuration, relaxed configuration and the associated adsorption energy. Atomic coordination values of the reported computational models are provided in the data repository (DOI 10.5258/SOTON/D0709).*

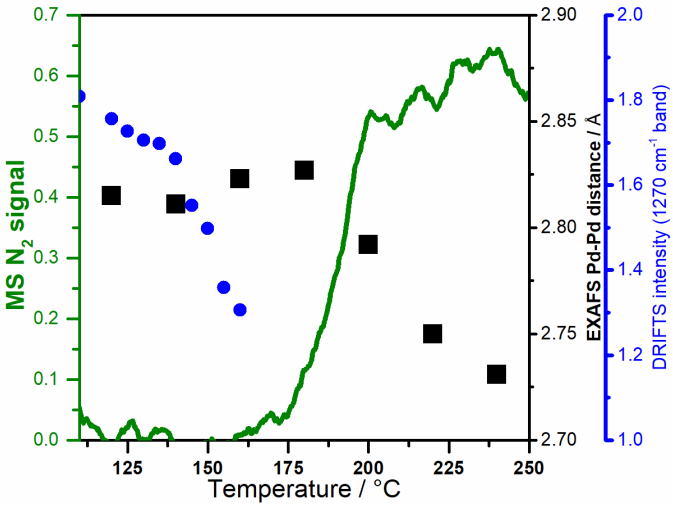
Initial configuration		Relaxed Configuration		E_{ad} / eV
		Top View	Side View	
$(NH_3)_{top}$ $(N_{top}$- $H_{HCP})$				-1.183
$(NH_3)_{top}$ $(N_{top}$- $H_{HCP})$				-1.185

$(NH_3)_{bdg}$ (Conf1)				**-1.187**
$(NH_3)_{bdg}$ (Conf2)				**-1.183**
$(NH_3)_{bdg}$ (Conf3)				**-1.186**
$(NH_3)_{hcp}$ (Conf1)				**-1.184**
$(NH_3)_{hcp}$ (Conf2)				**-1.189**

Supplementary Table 8. *Calculated adsorption energies of an NH_3 molecule adsorbed on Pd(111) surface away from an interstitial N-atom site in multiple configurations, showing initial configuration, relaxed configuration and the associated adsorption energy. Atomic coordination values of the reported computational models are provided in the data repository (DOI 10.5258/SOTON/D0709).*

Initial configuration		**Relaxed Configuration**		**E_{ad} / eV**
		Top View	**Side View**	
$(NH_3)_{top}$ (Conf1)				**-1.009**
$(NH_3)_{top}$ (Conf2)				**-1.005**

$(NH_3)_{hcp}$ (Conf1)				-1.007
$(NH_3)_{hcp}$ (Conf2)				-1.032
$(NH_3)_{bdg}$ (Conf1)				-1.005
$(NH_3)_{bdg}$ (Conf2)				-1.034



Supplementary Figure 22. *Overlay plot of Pd-Pd distance calculated from fitting models to Pd K-edge EXAFS data, N_2 signal from on-line mass spectrometry and intensity of asymmetric N-N stretching frequency from 1270 cm^{-1} DRIFTS absorption band plotted as a function of temperature.*

Supplementary Note 1. *Benchmark calculations on the use of 3x3x1 k-points.*

Benchmark calculations were used to check the effect of k-point grid density on the quality of computational results that are reported in this work. Monkhorst-Pack k-point grids with grid densities of 3x3x1, 5x5x1 and 7x7x1 were used to obtain average bond distances (Pd-Pd_{srf}, Pd-N and N-H) and adsorption energies (E_{ad}) for NH_3 on a Pd(111) surface with interstitial N. The relative bond distances and relative adsorption energies with respect to 3x3x1 k-point mesh show the negligible difference in the values obtained from different k-point grid densities for this particular system.

Supplementary Table 9. *Average bond distances and the adsorption energies as obtained from 3x3x1, 5x5x1 and 7x7x1 calculations. For convenience, the relative bond distances and relative adsorption energies with respect to 3x3x1 k-point mesh are also shown*

K-points	Average bond distances / Å						E_{ad} / eV	ΔE_{ad} / eV
	Pd-Pd_{Srf}	Δ(Pd-Pd_{srf})	Pd-N	Δ(Pd-N)	N-H	Δ(N-H)		
3x3x1	2.763	0.000	2.142	0.000	1.021	0.000	-1.033	0.000
5x5x1	2.765	0.002	2.149	0.007	1.021	0.000	-1.039	-0.006
7x7x1	2.764	0.002	2.150	0.008	1.021	0.000	-1.035	-0.002

Supplementary Note 2. *Benchmark Calculations on the use of partial occupancy value 0.2.*

The influence of the partial occupancy was checked between 0.05 eV – 0.2 eV, by calculating the difference in adsorption energies of NH_3 on Pd(111) surface.

Supplementary Table 10. *Smearing, and partial occupancy values used for calculating the adsorption energy of NH_3 on Pd(111) surface.*

System	Smearing	Partial occupancy / eV	E_{ad} / eV	Δ E_{ad} / eV
N_{top}-H_{HCP} on Pd(111)	1	0.200	-1.031	0.000
		0.100	-1.024	0.007
		0.050	-1.026	0.005