Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for the study: "Elucidating the Role of the State of Pd in the H_2-SCR of NOx by Operando XANES and DRIFTS"

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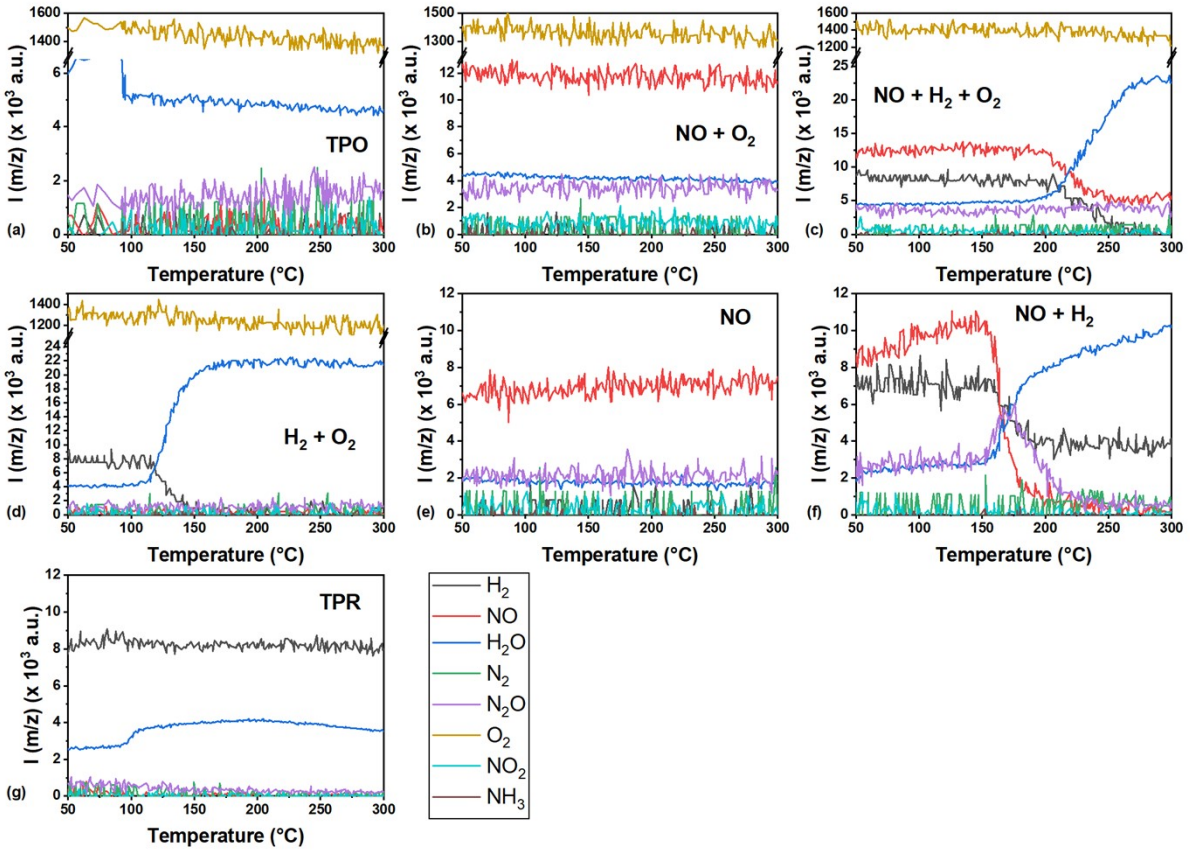

Figure S1. Light off curves showing H_2, NO, H_2O, N_2, N_2O, O_2, NO_2, and NH_3 (MS ion currents at m/z = 2, 30, 18, 28, 44, 32, 46, and 15, respectively, normalized to the signal for He m/z = 4) on the 1%Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst heated at 2 K/min under different gas mixtures containing 10% O_2, 5000 ppm H_2, and 1000 ppm NO (helium balance), presented in the order of introduction (a-g), with a 50 mL/min flow (GHSV 60,000 h^{-1}). Gas lines were flushed in inert gas between each measurement; the catalyst was reoxidized after the NO + H_2 mixture and before the TPR measurement.

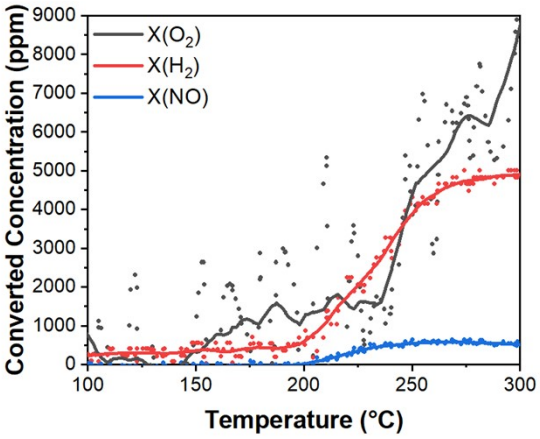

Figure S2. Light-off curves on 1%Pd/5%V_2O_5/20%TiO_2-Al_2O_3 heated at 2 K/min for the converted concentrations in ppm of H_2, NO, and O_2 calculated from MS data at m/z = 2, 30, and 32, respectively, under a 50 mL/min flow (GHSV 60,000 h^{-1}) of 1000 ppm NO, 5000 ppm H_2, and 10% O_2 in He. The dots are experimental data and the solid lines are locally weighted scatterplot smoothing (LOWESS) regressions.

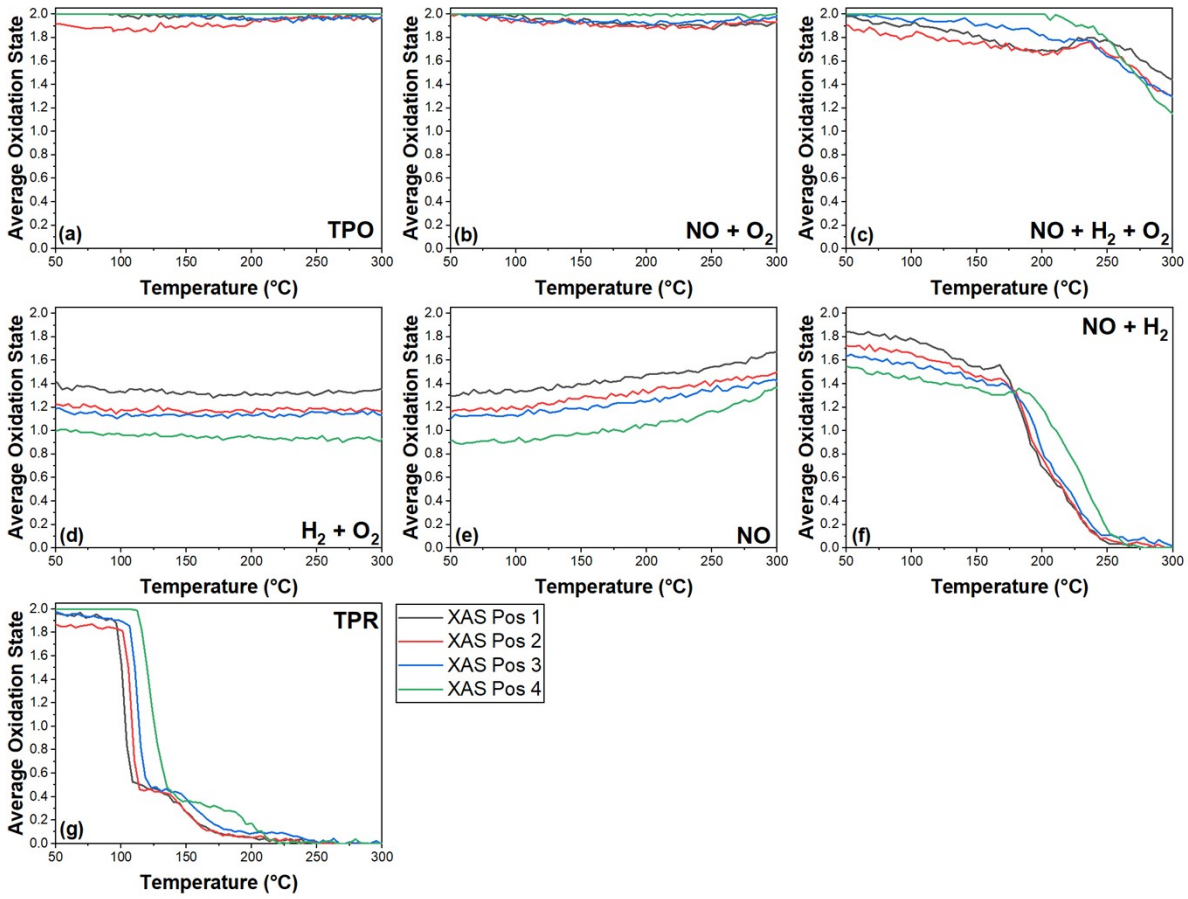

Figure S3 Space-resolved average Pd oxidation states according to LCA of XANES spectra (solid lines) on the 1%Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst heated at 2 K/min under different gas mixtures containing 10% O_2, 5000 ppm H_2, and 1000 ppm NO (helium balance), presented in the order of introduction (a-g), with a 50 mL/min flow (GHSV 60,000 h^{-1}). Gas lines were flushed in inert gas between each measurement; the catalyst was reoxidized after the NO + H_2 mixture and before the TPR measurement. Position 1 and 4 relate to the front and rear of the catalyst, respectively. Pt foil and PdO references were used for the LCA fits of the (a) TPO and (g) TPR measurements. LCA fits of all subsequent gas conditions.

In both the TPO (Figure S2a) and TPR (Figure S2g) gas mixtures, Pd fully oxidized and reduced, respectively, at all positions by 300 °C. With the co-adsorption of NO

and O_2 (Figure S2b), Pd started fully oxidized at 50 °C, following the TPO measurement, and very slightly reduced at all positions with increasing temperature, with exception to the rear of the catalyst bed which remained fully oxidized. In the mixture of O_2 and H_2 (Figure S2d), there was no significant net change in oxidation state at any probed position, despite the 40x over-stoichiometric presence of O_2 required for H_2 combustion; here the catalyst started in a slightly reduced state, because the gas lines were flushed with inert gas after the SCR mixture, but the catalyst was not fully reoxidized. In NO (Figure S2e), Pd gradually oxidized in small amounts with increasing temperature with the rear position, due to starting more reduced, oxidizing more significantly than other positions; here the starting oxidation states of Pd were retained from the O_2 and H_2 mixture. The XANES results of the NO and H_2 (Figure S2c) and SCR (Figure S2f) mixtures are discussed in the main text.

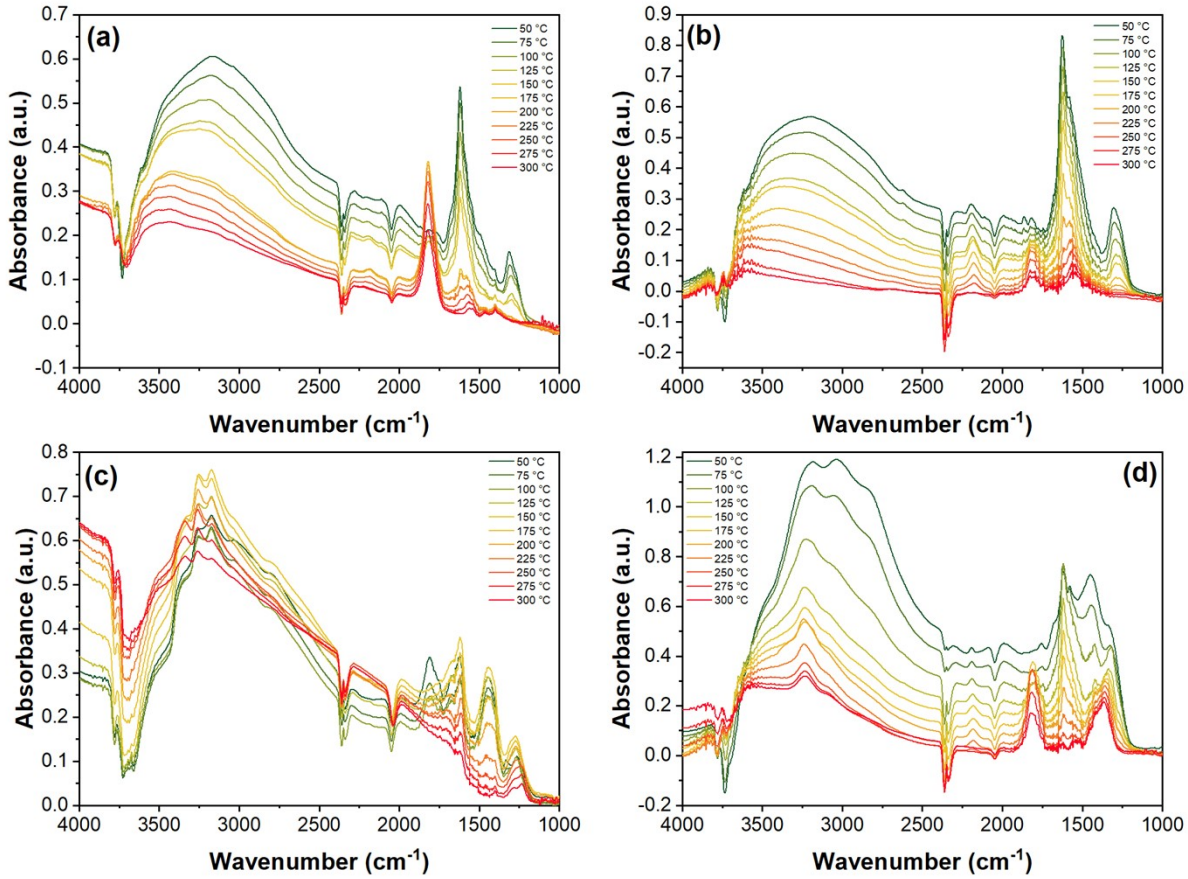

Figure S4. Temperature dependent DRIFTS spectra without any baseline correction of the 1%Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst under a flow of (a) 1000 ppm NO in argon, (b) 1000 ppm NO and 10% O_2 in Ar, (c) 1000 ppm NO and 5000 ppm H_2 in argon, and (d) 1000 ppm NO, 5000 ppm H_2, and 10% O_2 in Ar.

Table S1. Extended X-Ray absorbance fine structure fitted parameters for the 1%Pd/5%V_2O_5/20%TiO_2-Al_2O_3 catalyst

Sample	d Pd-Pd (Å)	Coordination Number	σ^2 (Pd) (10^{-3} Å^2)	δE_0 (eV)	ρ (%)
Pd Foil	2.737 ± 0.002	12*	5.2 ± 0.3	3.4 ± 0.3	0.1
Catalyst	2.74 ± 0.02	8.1 ± 1.5	9.4	-0.1 ± 2.1	1.2

* Amplitude reduction factor determined as 0.83