Electronic Supporting Information (ESI)

Structural Selectivity of Supported Pd Nanoparticles: Selective Ethanol Ammoxidation to Acetonitrile

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1. XAS measurements

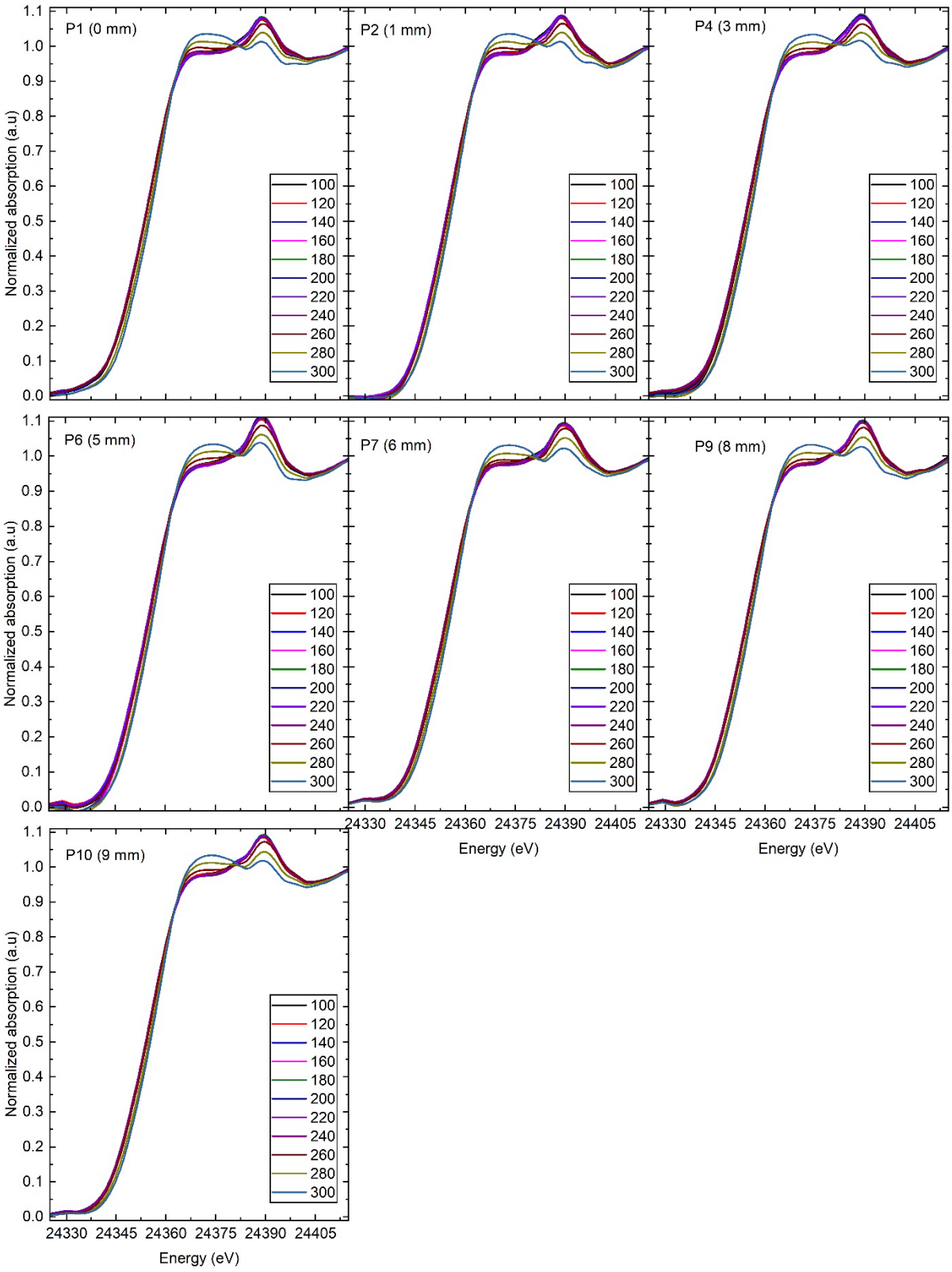


Figure S1. Normalized XANES spectra at the Pd K-edge, captured at various positions along the catalyst bed during ethanol ammoxidation. Measurements were conducted isothermally across a temperature range of 100–300 °C, as indicated.

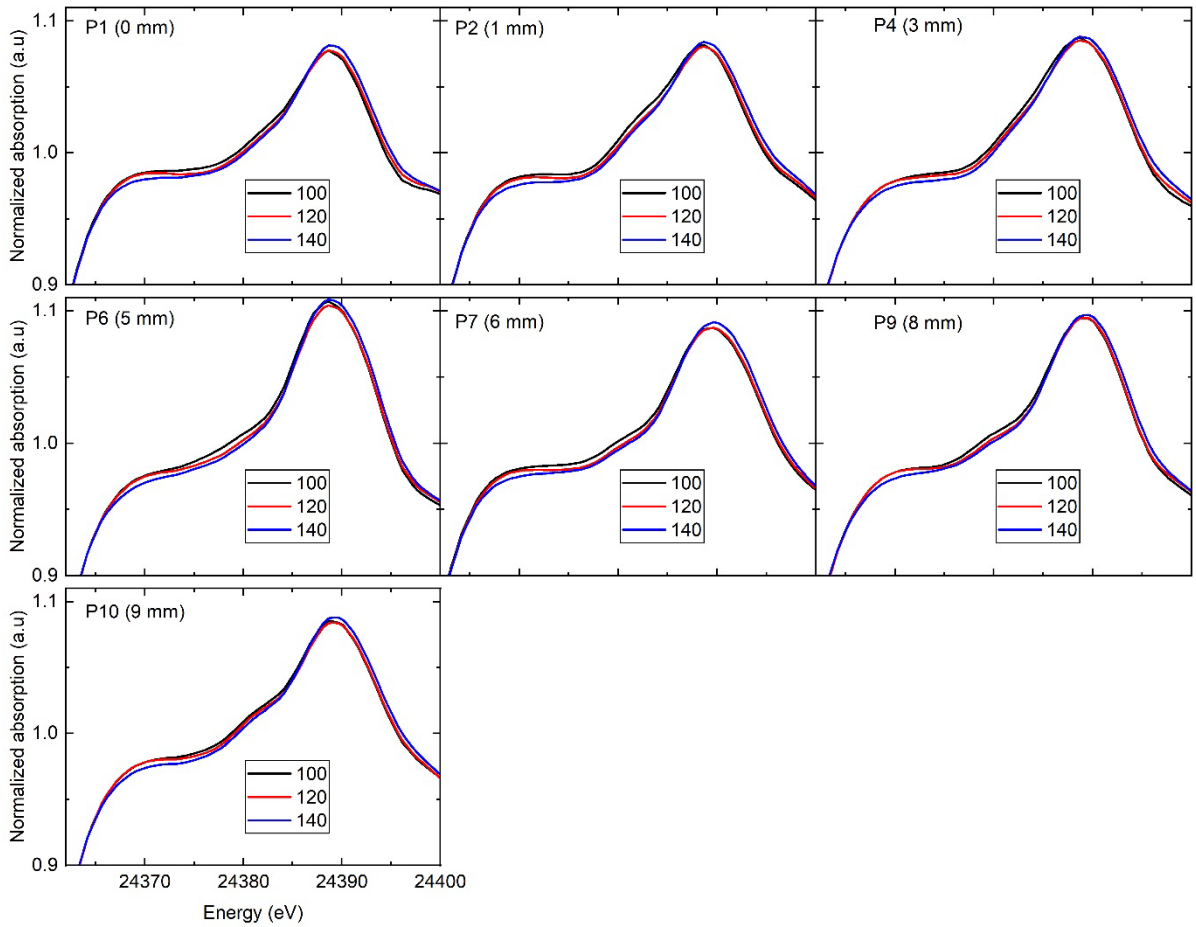


Figure S2. Magnified view of the XANES spectra (100 – 140 °C) focusing on specific regions to detect potential signatures of PdN_x PdC_x phases that may emerge during the reaction.

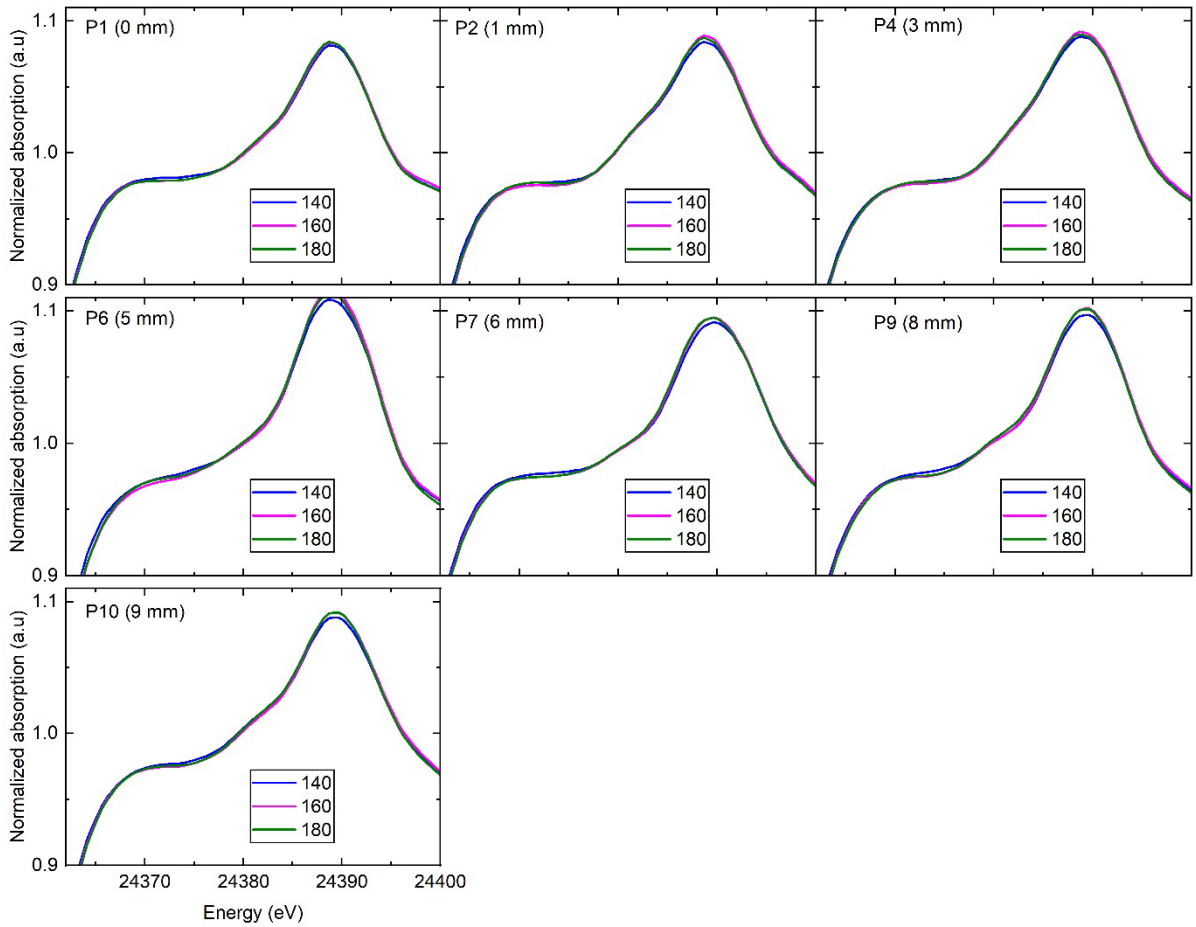


Figure S3. Magnified view of the XANES spectra (140 – 180 °C) focusing on specific regions to detect potential signatures of PdN_x PdC_x phases that may emerge during the reaction.

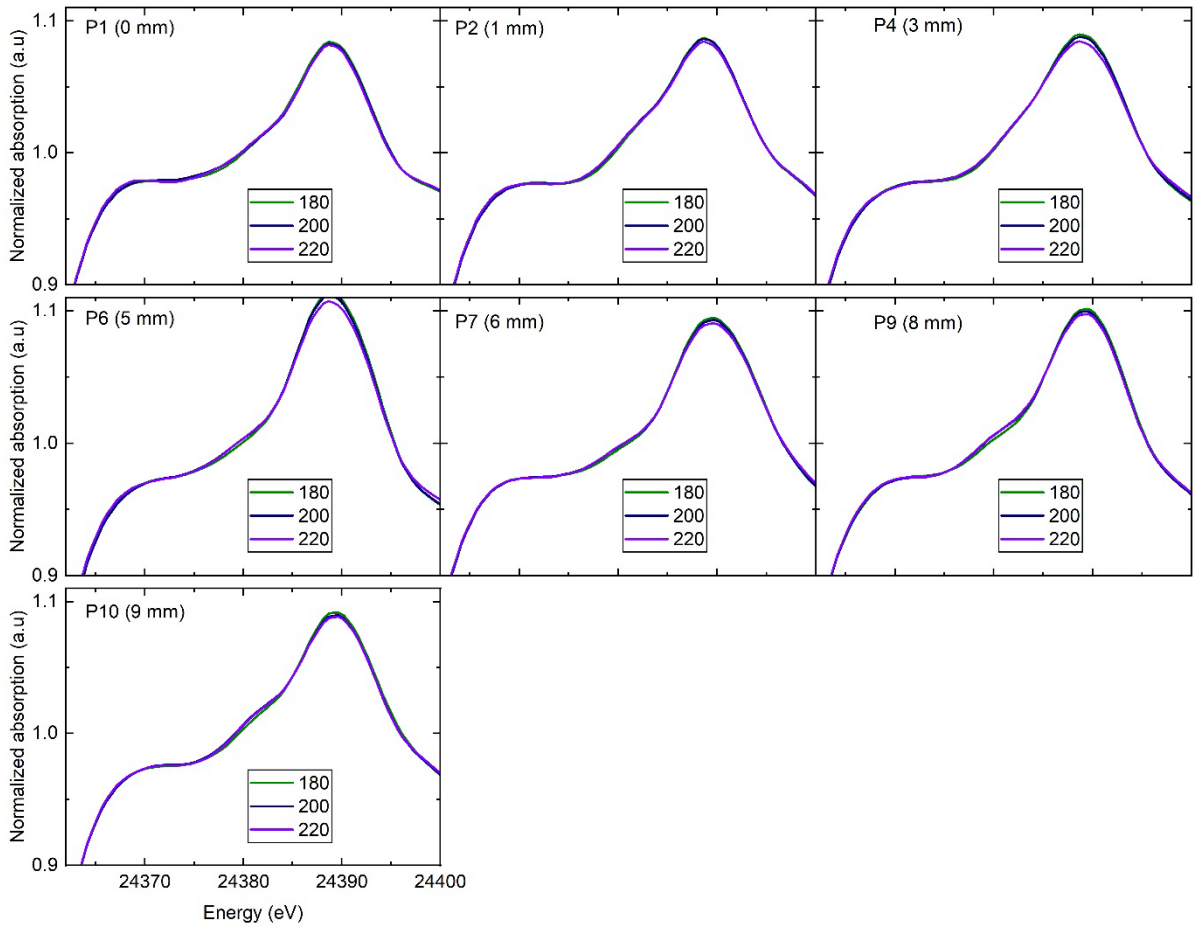


Figure S4. Magnified view of the XANES spectra (180 – 220 °C) focusing on specific regions to detect potential signatures of PdN_x PdC_x phases that may emerge during the reaction.

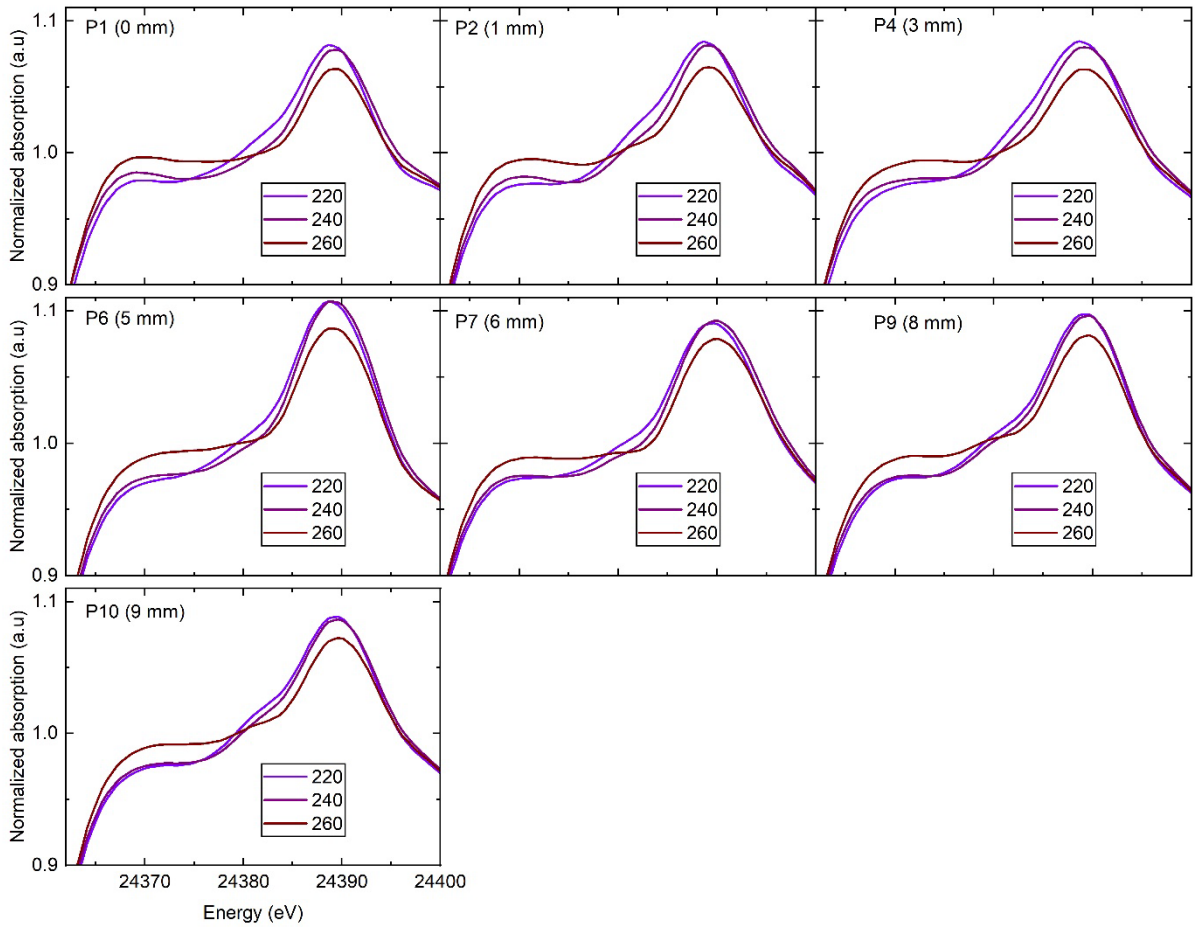


Figure S5. Magnified view of the XANES spectra (220 – 260 °C) focusing on specific regions to detect potential signatures of PdN_x PdC_x phases that may emerge during the reaction.

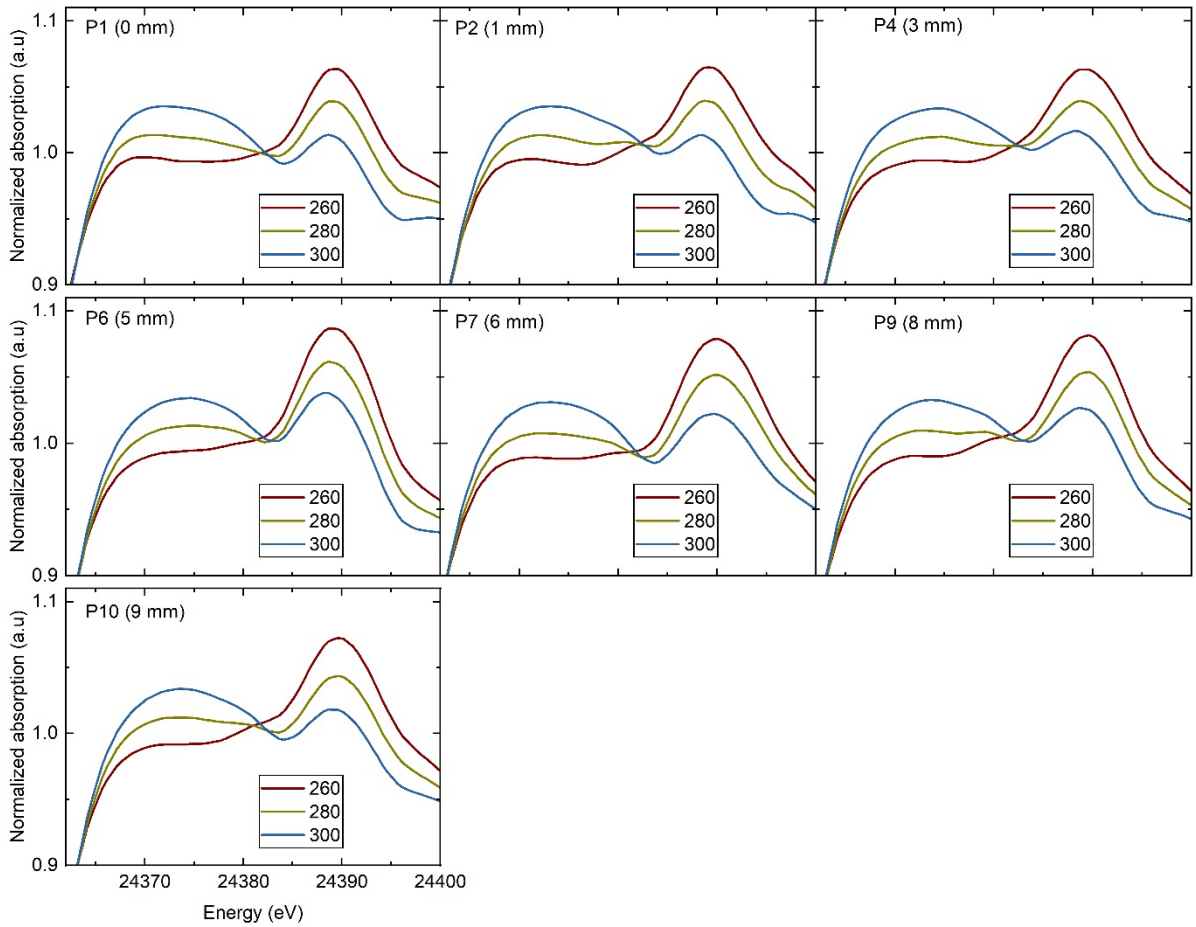


Figure S6. Magnified view of the XANES spectra (260 – 300 ℃) focusing on specific regions to detect potential signatures of PdN_x PdC_x phases that may emerge during the reaction.

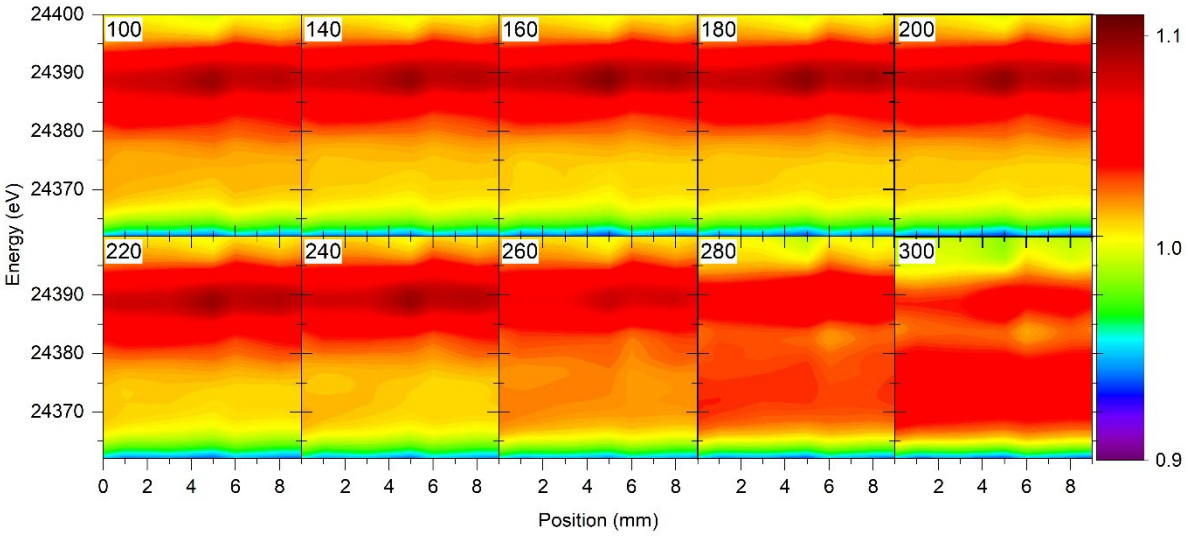


Figure S7. 3D contour plots at various temperatures, as indicated, derived from the spectra showcased in Figures S2-S6, to trace any variations along the catalyst bed.

2. *Ex situ* XAFS data

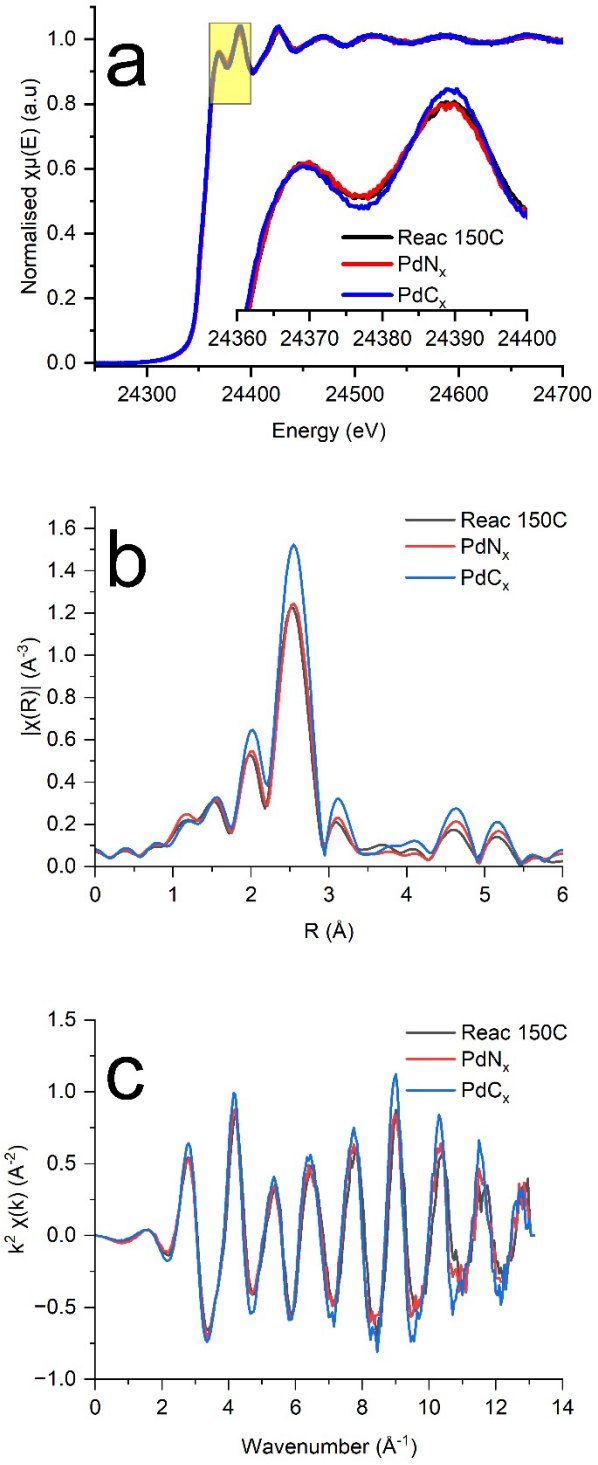
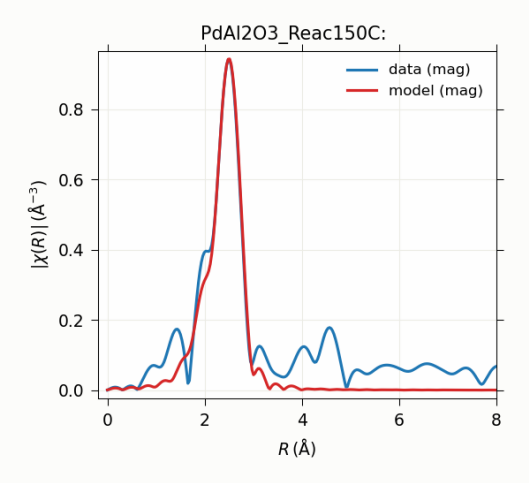
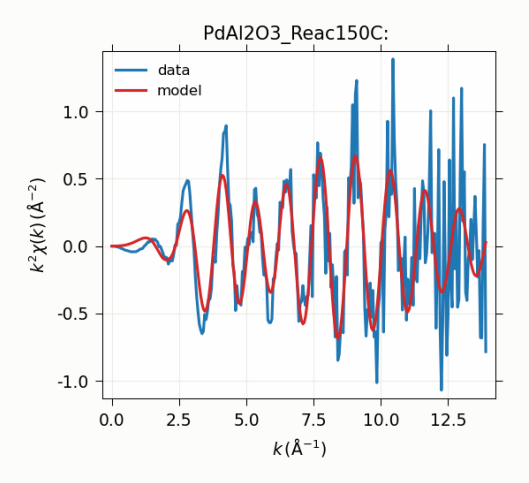
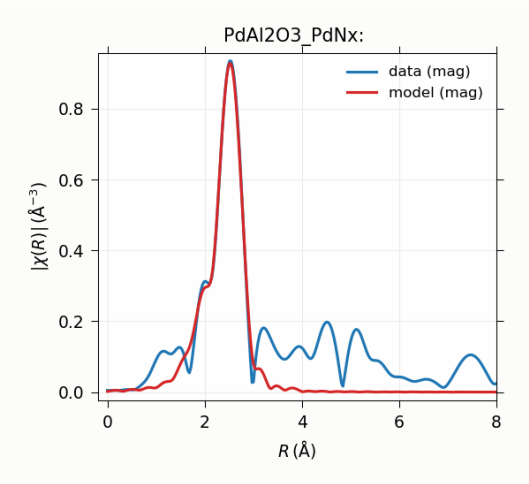


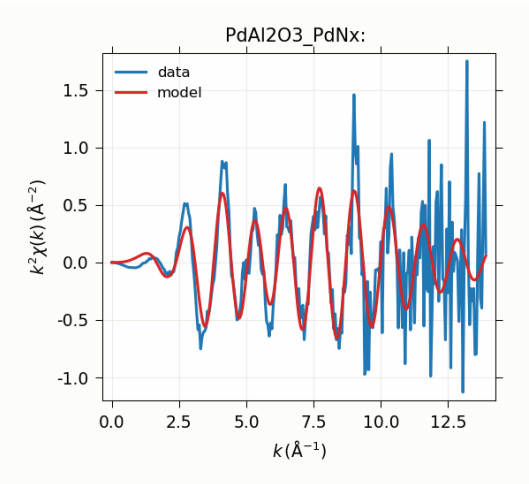
Figure S8. Comparative analysis of Pd K-edge XAFS spectra: (a) Normalized spectra, (b) Corresponding Fourier transform, and (c) k^2-weighted χ(k) data for PdNx, PdCx, and the catalyst post-use at 150°C.



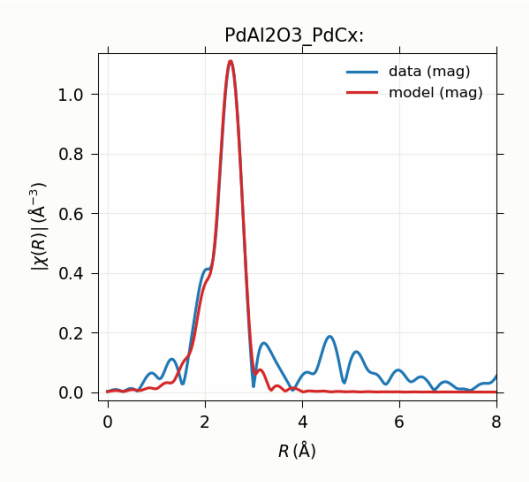


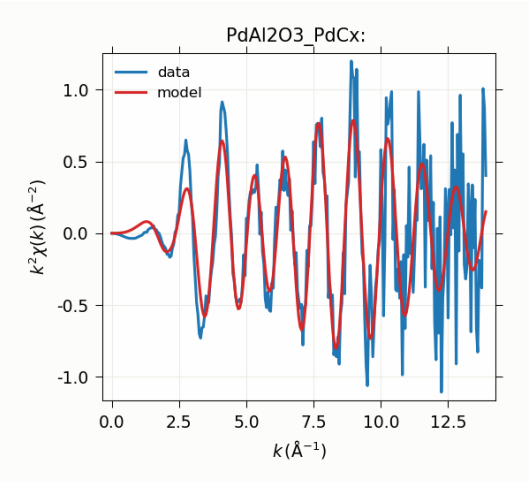
a) Used catalyst at 150C: r space (left), k^2 weight (right)





b) PdN_x: r space (left), k^2 weight (right)





c) PdC_x: r space (left), k^2 weight (right)

Figure S9. Ex-situ Pd K-edge EXAFS spectra and their corresponding fits (non-phase corrected) in Fourier-Transformed (left) and k^2-weighted (right) space of 1.5wt% Pd/γ-Al_2O_3 samples: a) used at 150°C, b) PdN_x phase, and c) PdC_x phase.

Table S1. EXAFS fitting parameters for the Pd K-edge spectra of 1.5 wt% Pd/Al_2O_3 catalyst used at 150°C, alongside the nitridised (PdN_x) and carbidised (PdC_x) samples.

Sample	CN (Pd-Pd)	$sigma^2$	E_0 (eV)	R (Å)	R factor
used at 150C	6.2 (1.1)	0.0068 (16)	-6.3(1.7)	2.778(10)	0.034
PdNx	7.6(1.6)	0.0084 (15)	-6.2(1.6)	2.789(10)	0.121
PdCx	7.9(1.1)	0.0071(7)	-5.9(0.8)	2.799(5)	0.009

* Fitted from one scattering path of the absorbing Pd atom to the nearest neighbour Pd atoms (Pd-Pd), using $S0^2 = 0.8$ as determined using a Pd foil standard; Fit range $3 < k$ ($Å^{-2}$) < 11.9, $1 < R$ / Å < 3.

3. SEM Characterisation

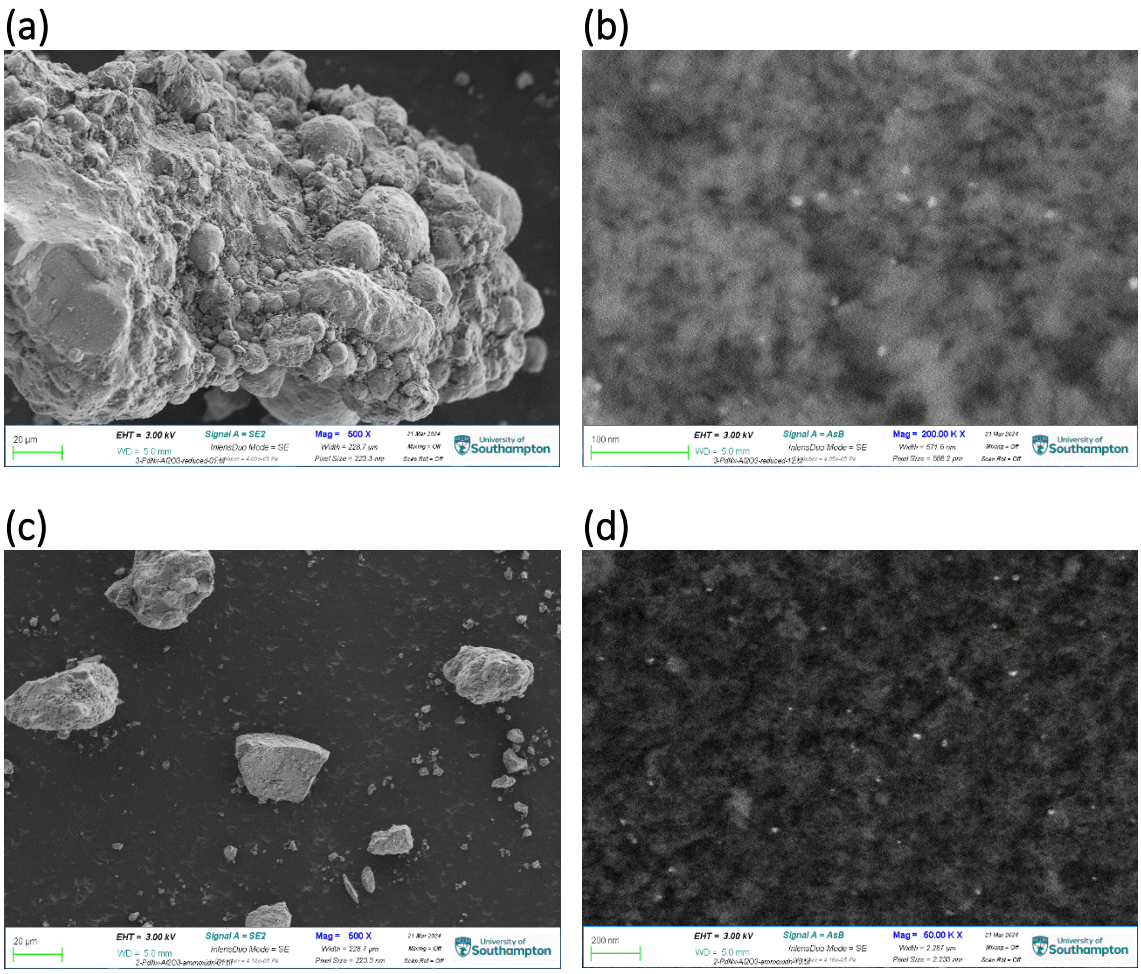


Figure S10. SEM images of fresh (Figure S10a and b) and spent – i.e., post ammoxidation - (Figure S10c and d) 1.5wt% Pd/γ-Al_2O_3 catalyst.

4. Ethanol pulse testing

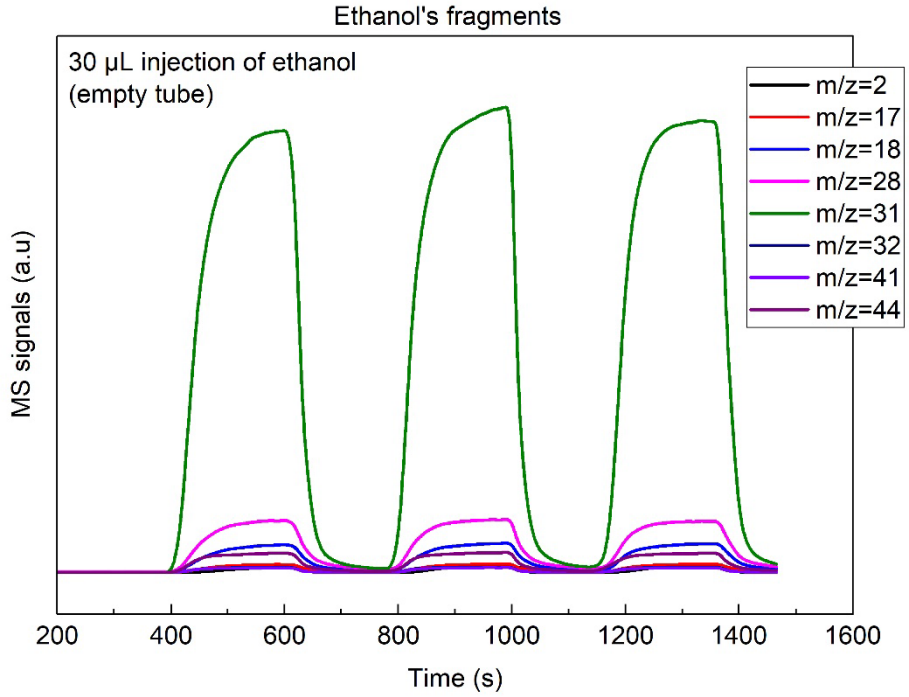


Figure S11. 30 µL injection of ethanol in an empty to trace any fragments of m/z = Traces of m/z = 2, 17, 18, 28, 31, 32, 41, and 44. Injection was performed 3 times.

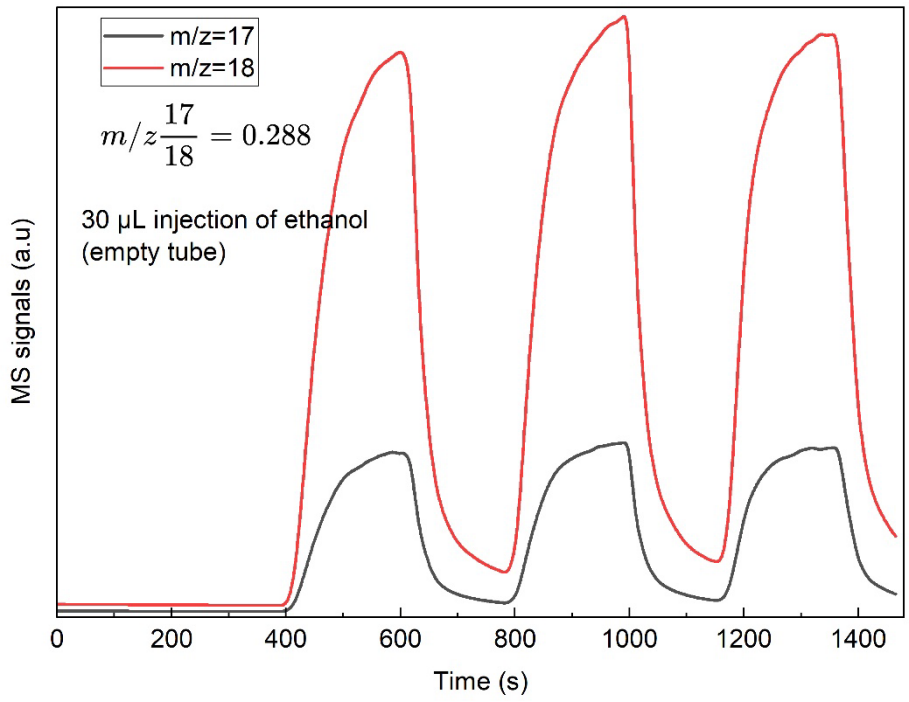


Figure S12. Same data presented in Figure S10 above but here we show only traces of m/z = 17 and 18 when 30 µL of ethanol was injected in an empty. Injection was performed 3 times with an average m/z(17/18) ratio of 0.288.

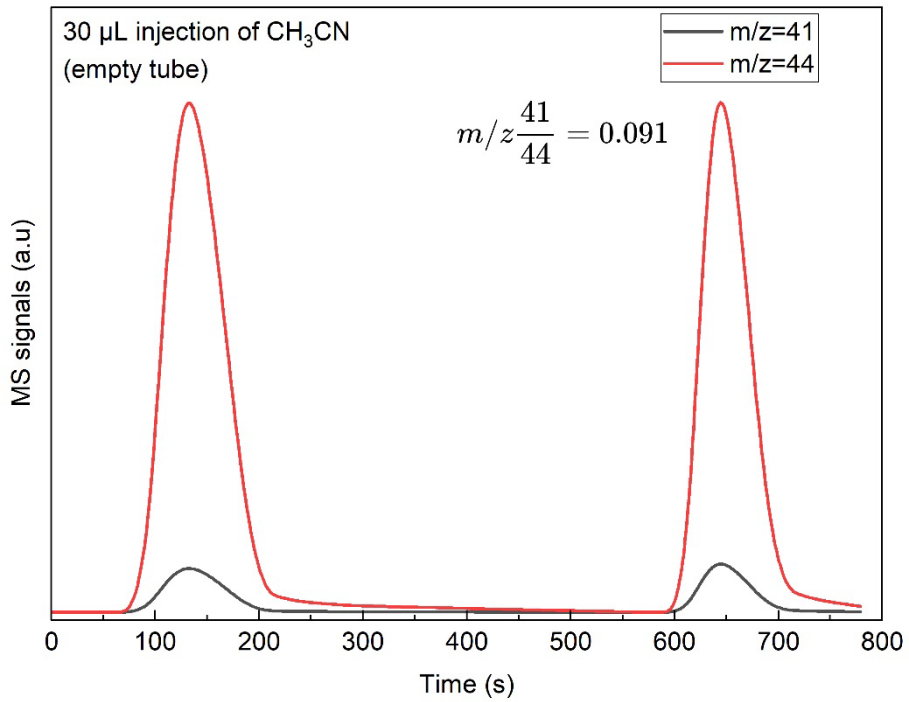


Figure S13. Traces of m/z = 41 and 44 when 30 µL of acetaldehyde was injected in an empty. Injection was performed 2 times with an average of m/z (41/44) ratio of 0.091.