1 In situ valence modification of Pd/NiO nano-catalysts in

2 supercritical water towards toluene oxidation

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16 **Fig. S1** (a) Schematic representation of the three-pump (P1–P3) continuous 17 hydrothermal flow synthesis system that was used to prepare nanoparticles catalysts. 18 Key: P = pump, BPR = back-pressure regulator, R = reactor, H = heater, T = T19 junction; (b) Schematic diagram of the confined jet reactor (R. I. Gruar, C. J. Tighe 20 and J. A. Darr, Industrial & Engineering Chemistry Research, 2013, 52, 5270-5281).



Fig. S2 HR-TEM image of sc-NiO(left), sc-Pd/NiO(middle) and sc-Pd/NiO-R(right) catalyst where (a) represents the d-spacing of NiO and (b) shows a fast Fourier transform pattern of NiO.



27 Fig. S3 HAADF-STEM images of palladium in sc-Pd/NiO catalyst (b); cyan
28 dots/rods in (a) represent the palladium atoms as projected by EDS mapping.



Fig. S4 The CO₂ evolution rates of (a) sc-0.43Pd/NiO-R and (b) sc-0.48Pd/NiO-H₂ for toluene oxidation.*Condition: toluene (500 ppm), O₂ (10 vol.%), 0.5 g catalyst, GHSV = 19200 mL g_{cat}^{-1} h⁻¹. The plot showed that the sample synthesized by using supercritical water exhibited low-temperature CO₂ conversions, ca. 20 °C lower than that by post-treatment in H₂.

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37 Fig. S5 DRIFT spectra of sc-NiO catalyst in toluene stream at 30 °C.



39 Fig. S6 Pd3d XPS spectra of aged sc-Pd/NiO-R.



41 Fig. S7 The plot of pulse hydro-oxygen titration over sc-Pd/NiO catalyst.

42 *Condition: 300 °C for 2h under 6 vol.% H_2/N_2 at a flow of 30 mL min⁻¹, 0.1 g 43 catalyst.



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45 **Fig. S8** Catalytic activity of sc-Pd/NiO-R for toluene oxidation in terms of toluene 46 removal rates and CO₂ evolution rates when ageing at 190 °C and 200 °C for 25 h. 47 *Condition: toluene (500 ppm), O₂ (10 vol.%), 0.5 g catalyst, GHSV = 19200 mL g_{cat}-48 ¹ h⁻¹.



50 Fig. S9 The water-resistant ability of sc-Pd/NiO-R for toluene oxidation in the 51 presence of 5 vol% water vapour in terms of durable activity after repeated cycles and 52 isothermal ageing at 194 °C for 25h. *Condition: toluene (500 ppm), O₂ (10 vol%), 53 0.5 g catalyst, GHSV = 19200 mL g_{cat}^{-1} h⁻¹.