In situ valence modification of Pd/NiO nano-catalysts in supercritical water towards toluene oxidation

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**Fig. S1** (a) Schematic representation of the three-pump (P1–P3) continuous hydrothermal flow synthesis system that was used to prepare nanoparticles catalysts. Key: P = pump, BPR = back-pressure regulator, R = reactor, H = heater, T = T junction; (b) Schematic diagram of the confined jet reactor (R. I. Gruar, C. J. Tighe 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.
Fig. S3  HAADF-STEM images of palladium in sc-Pd/NiO catalyst (b); cyan dots/rods in (a) represent the palladium atoms as projected by EDS mapping.

Fig. S4  The CO\textsubscript{2} evolution rates of (a) sc-0.43Pd/NiO-R and (b) sc-0.48Pd/NiO-H\textsubscript{2} for toluene oxidation.*Condition: toluene (500 ppm), O\textsubscript{2} (10 vol.%), 0.5 g catalyst, GHSV = 19200 mL g\textsuperscript{-1} h\textsuperscript{-1}. The plot showed that the sample synthesized by using supercritical water exhibited low-temperature CO\textsubscript{2} conversions, ca. 20 °C lower than that by post-treatment in H\textsubscript{2}.
**Fig. S5** DRIFT spectra of sc-NiO catalyst in toluene stream at 30 °C.

**Fig. S6** Pd3d XPS spectra of aged sc-Pd/NiO-R.
Fig. S7 The plot of pulse hydro-oxygen titration over sc-Pd/NiO catalyst.

*Condition: 300 °C for 2h under 6 vol.% H₂/N₂ at a flow of 30 mL min⁻¹, 0.1 g catalyst.

Fig. S8 Catalytic activity of sc-Pd/NiO-R for toluene oxidation in terms of toluene removal rates and CO₂ evolution rates when ageing at 190 °C and 200 °C for 25 h.

*Condition: toluene (500 ppm), O₂ (10 vol.%), 0.5 g catalyst, GHSV = 19200 mL g⁻¹ h⁻¹.
**Fig. S9** The water-resistant ability of sc-Pd/NiO-R for toluene oxidation in the presence of 5 vol% water vapour in terms of durable activity after repeated cycles and isothermal ageing at 194 °C for 25h. *Condition: toluene (500 ppm), O$_2$ (10 vol%), 0.5 g catalyst, GHSV = 19200 mL g$^{-1}$ h$^{-1}$. 

![Graph showing CO$_2$ conversion vs. temperature and time with ageing at 194°C and 5 vol% H$_2$O]