Supporting Information for:

Bimetallic Pt-Ni composites on ceria-doped alumina supports as catalysts in the aqueous-phase reforming of glycerol

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1. N\textsubscript{2} physisorption isotherms
Figure S1. N$_2$ physisorption isotherms of Pt/Al$_2$O$_3$ and Pt/CeO$_2$-Al$_2$O$_3$ catalysts. Isotherms were collected on an Autosorb iQ instrument (Quantachrome) at −196 °C.

2. Scanning electron micrographs

Figure S2. Scanning electron micrographs of (a) 1Pt/3CeAl and (b) 1Pt-18Ni/3CeAl.
3. Transmission electron microscope images

Figure S3. Transmission electron images of (a) 1Pt-6Ni/3CeAl and (b) 1Pt-18Ni/3CeAl catalysts reduced in flowing H2 (50 vol.% with N2) at 800 °C for 60 min (heating rate of 1.5 °C min⁻¹).

4. APR apparatus

Figure S4. Schematic of apparatus used for APR studies.
5. GC calibration curves

![GC calibration curves for hydrogen, methane and carbon dioxide.](image)

Figure S5. GC calibration curves for hydrogen, methane and carbon dioxide.

6. A representative GC curve

![A representative GC curve from the APR of glycerol over 1Pt-12Ni/3CeAl, as measured on the in-line Varian CP-3800 gas chromatograph. The product gas was sampled every 25 min; three successive injections are shown here.](image)

Figure S6. A representative GC curve from the APR of glycerol over 1Pt-12Ni/3CeAl, as measured on the in-line Varian CP-3800 gas chromatograph. The product gas was sampled every 25 min; three successive injections are shown here.
7. HPLC calibration curve and a representative curve

Figure S7. (a) HPLC calibration curve for glycerol; and (b) a representative HPLC analysis of the liquid product of APR over 1Pt-6Ni/3CeAl (240 °C, 40 bar, 1 wt% glycerol, 0.05 mL min⁻¹, 250 mg catalyst).

8. Energy-dispersive X-ray spectra of a Pt-Ni/3CeAl catalyst

Figure S8. Energy-dispersive X-ray spectra of three spots on a 1Pt-18Ni/3CeAl catalyst that was reduced in flowing H₂ (50 vol% in N₂) at 800 °C for 60 min (heating rate 1.5 °C min⁻¹).
9. Ce 3d and Pt 4d$_{5/2}$ regions of the X-ray photoelectron spectra of fresh catalysts

Figure S9 The Ce 3d region of the X-ray photoelectron spectra of xPt-yNi/3CeAl catalysts after reduction in flowing H$_2$ (50 vol.% in N$_2$) at 800 °C for 60 min (heating rate 1.5 °C min$^{-1}$).

Figure S10. The Pt 4d$_{5/2}$ regions of the X-ray photoelectron spectra of 1Pt-yNi/3CeAl composites after reduction in flowing H$_2$ (50 vol.% in N$_2$) at 800 °C for 60 min (heating rate 1.5 °C min$^{-1}$). Baselines have been subtracted. No high-resolution spectrum of this region was obtained for sample 1Pt/3CeAl.
10. X-ray diffraction patterns of fresh and spent catalysts

**Figure S11.** XRD patterns of catalysts freshly reduced in flowing H₂ (50 vol% in N₂) at 800 °C for 60 min, and of the spent catalysts after 30 h on stream in the APR of glycerol (240 °C, 40 bar, 1 wt% glycerol, 0.05 mL/min, 250 mg catalyst).
11. TGA curves
Figure S12. TGA analysis of (a) Fresh 1Pt-18Ni/3CeAl (b) Spent 1Pt-18Ni/3CeAl (c) Fresh 1Pt-12Ni/3CeAl (d) Spent1Pt-12Ni/3CeAl (e) Fresh 1Pt-3Ni/3CeAl (f) Spent 1Pt-3Ni/3CeAl (g) Fresh 6Ni/3CeAl (h) Spent 6Ni/3CeAl (i) Spent mixture of separate Pt/3CeAl and Ni/3CeAl catalysts with a total of 1 wt% Pt and 6 wt% Ni. In all cases, Fresh = catalysts freshly reduced in flowing H₂ (50 vol% in N₂) at 800 °C for 60 min, and Spent = spent catalyst after ≥30 h on stream in the APR of glycerol (240 °C, 40 bar, 1 wt% glycerol, 0.05 mL min⁻¹, 250 mg catalyst). Samples were heated at 10 °C/min under instrument air (40 mL/min).
12. X-ray photoelectron spectra of spent catalysts

Figure S13 The C 1s region of the X-ray photoelectron spectra of xPt-yNi/3CeAl composites before and after use as catalysts in the aqueous phase reforming of glycerol for 30 h (6Ni/CeAl and 1Pt-18Ni/3CeAl) or 85 h (1Pt-6Ni/3CeAl). Traces for each sample were normalised to the intensity of the experimental trace, so intensities cannot be compared among samples. Spent catalysts were referenced to have the same Al 2p binding energy as the corresponding fresh catalyst.
Figure S14. The (a) Al 2p and Pt 4f, and (b) Ni 2p₃/₂ regions of the X-ray photoelectron spectra of 1Pt-yNi/3CeAl composites before and after use as catalysts in the aqueous phase reforming of glycerol for 30 h (6Ni/CeAl and 1Pt-18Ni/3CeAl) or 85 h (1Pt-6Ni/3CeAl). Traces for each sample were normalised, so intensities cannot be compared among samples.