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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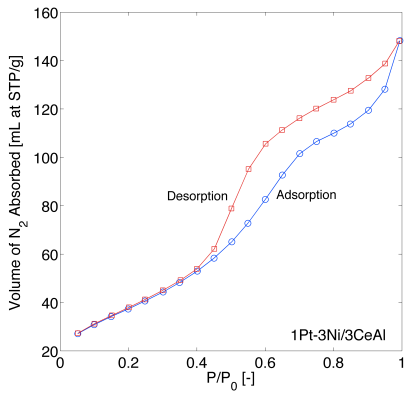
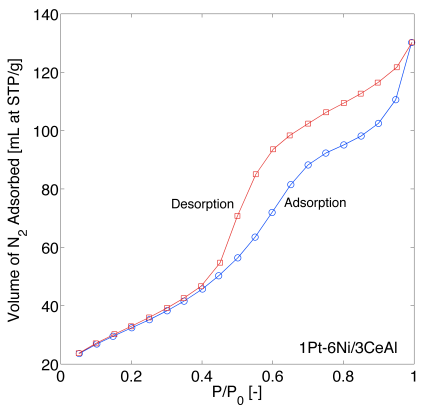
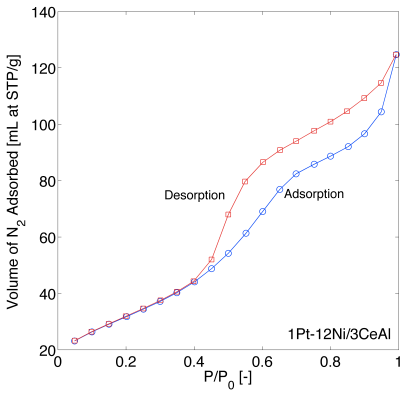
1. N_2 physisorption isotherms







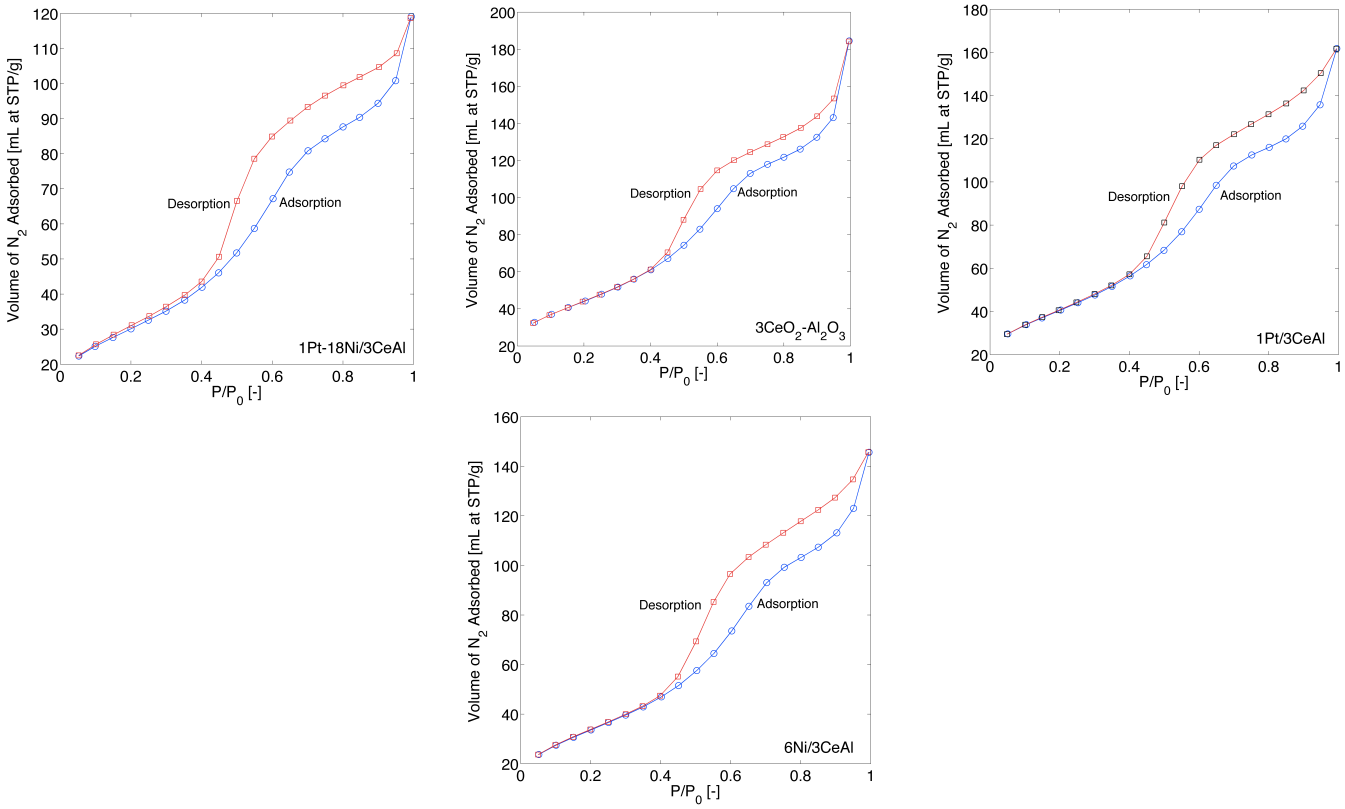


Figure S1. N_2 physisorption isotherms of Pt/Al_2O_3 and Pt/CeO_2-Al_2O_3 catalysts. Isotherms were collected on an Autosorb iQ instrument (Quantachrome) at −196 °C.

2. Scanning electron micrographs

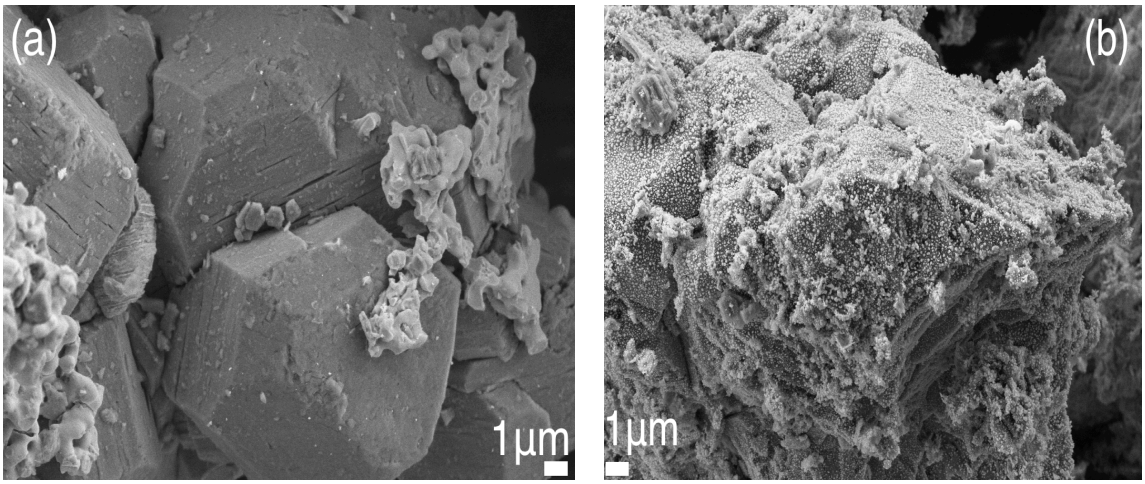


Figure S2. Scanning electron micrographs of (a) 1Pt/3CeAl and (b) 1Pt-18Ni/3CeAl.

3. Transmission electron microscope images

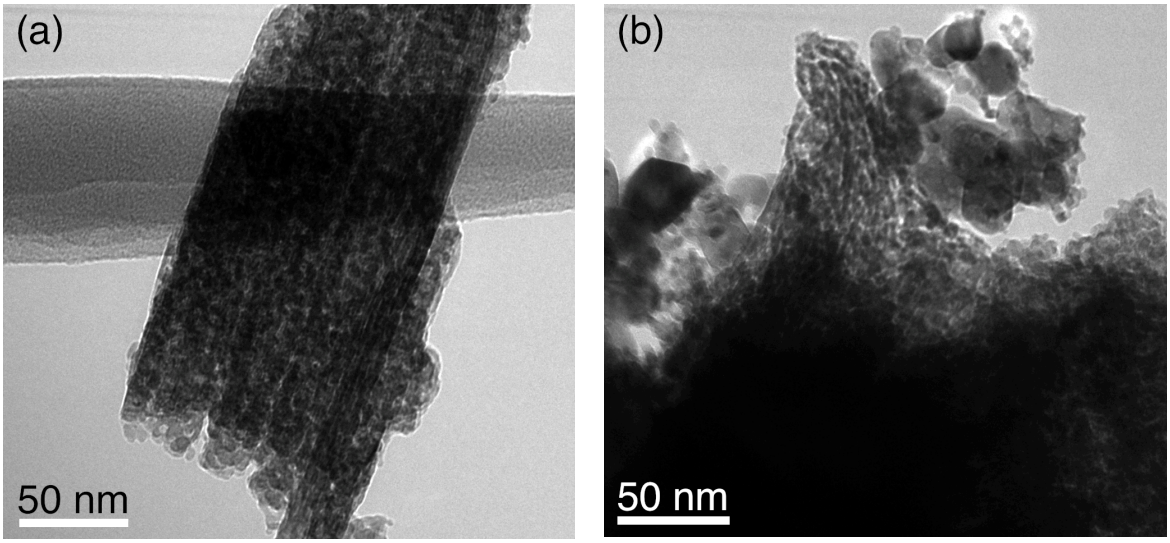


Figure S3. Transmission electron images of (a) 1Pt-6Ni/3CeAl and (b) 1Pt-18Ni/3CeAl catalysts reduced in flowing H2 (50 vol.% with N_2) at 800 °C for 60 min (heating rate of 1.5 °C min^{-1}).

4. APR apparatus

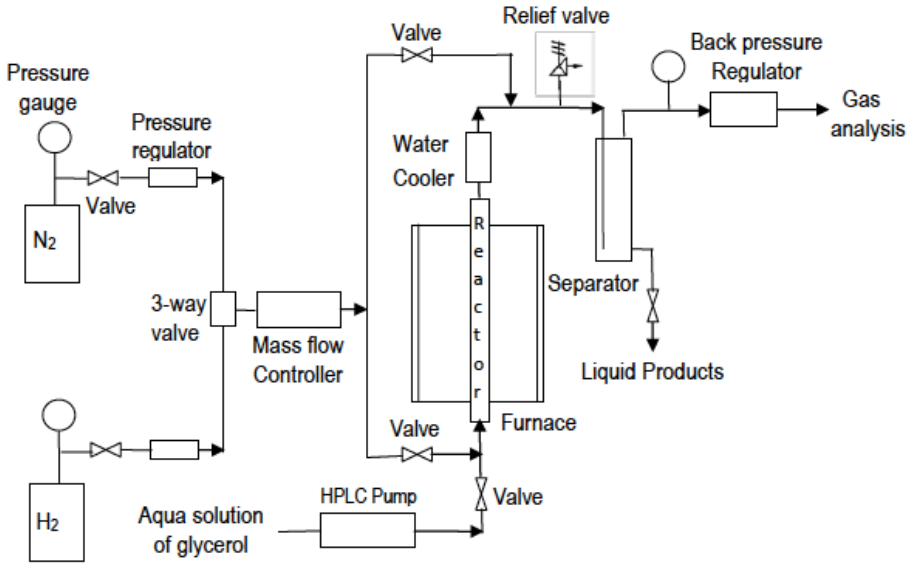


Figure S4. Schematic of apparatus used for APR studies.

5. GC calibration curves

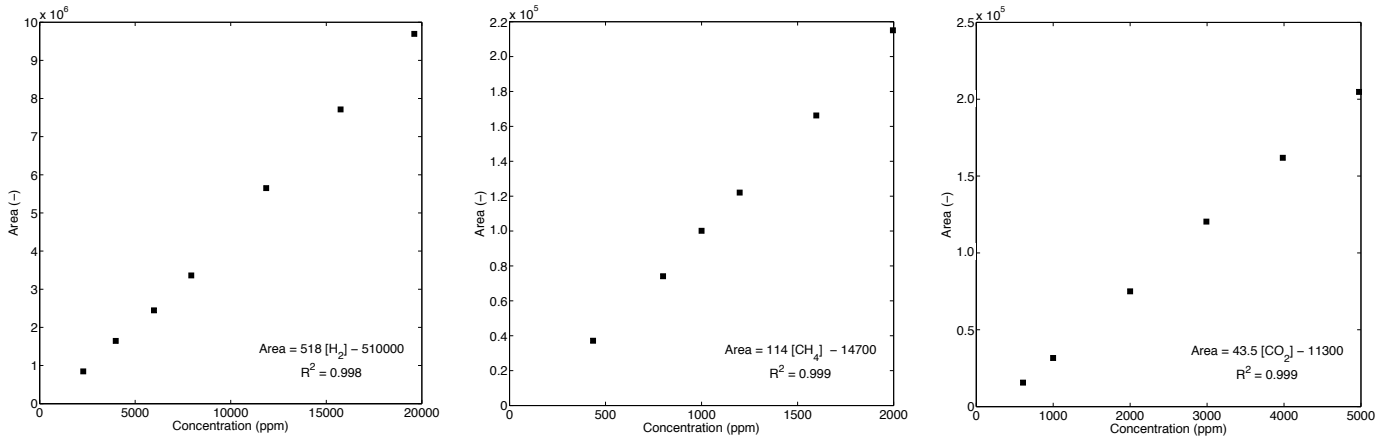


Figure S5. GC calibration curves for hydrogen, methane and carbon dioxide.

6. A representative GC curve

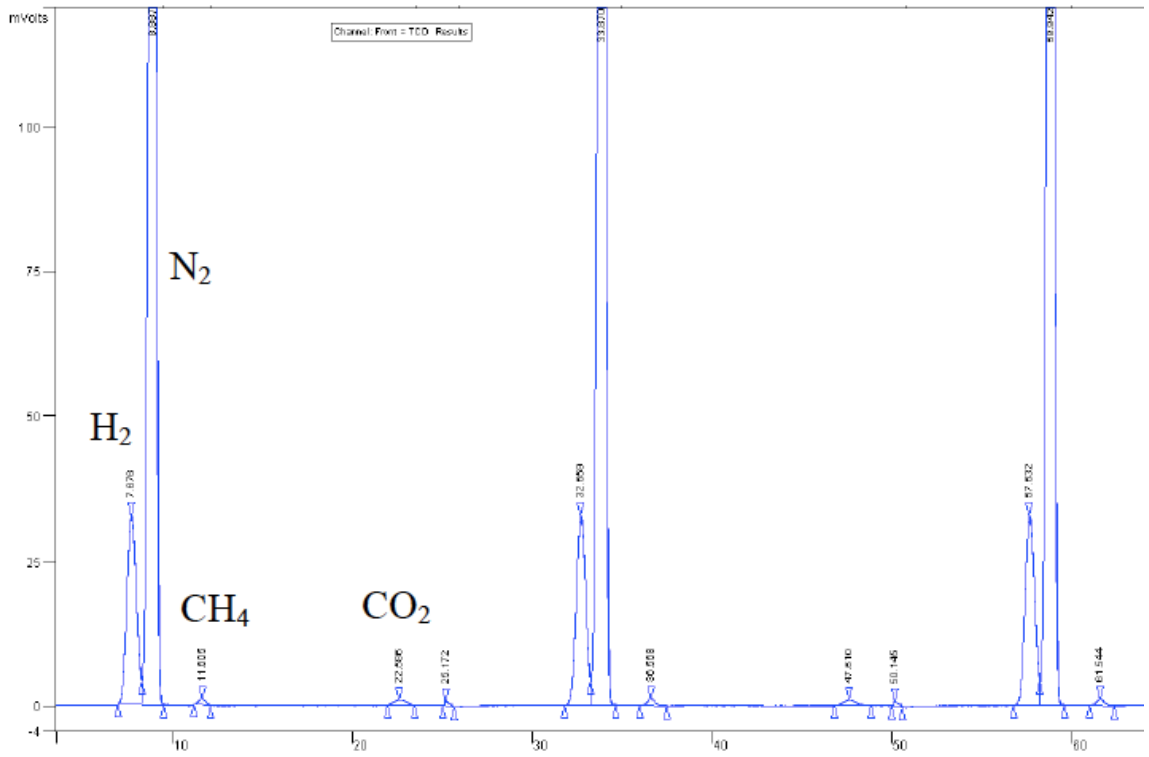


Figure S6. A representative GC curve from the APR of glycerol over 1Pt-12Ni/3CeAl, as measured on the in-line Varian CP-3800 gas chromatograph. The product gas was sampled every 25 min; three successive injections are shown here.

7. HPLC calibration curve and a representative curve

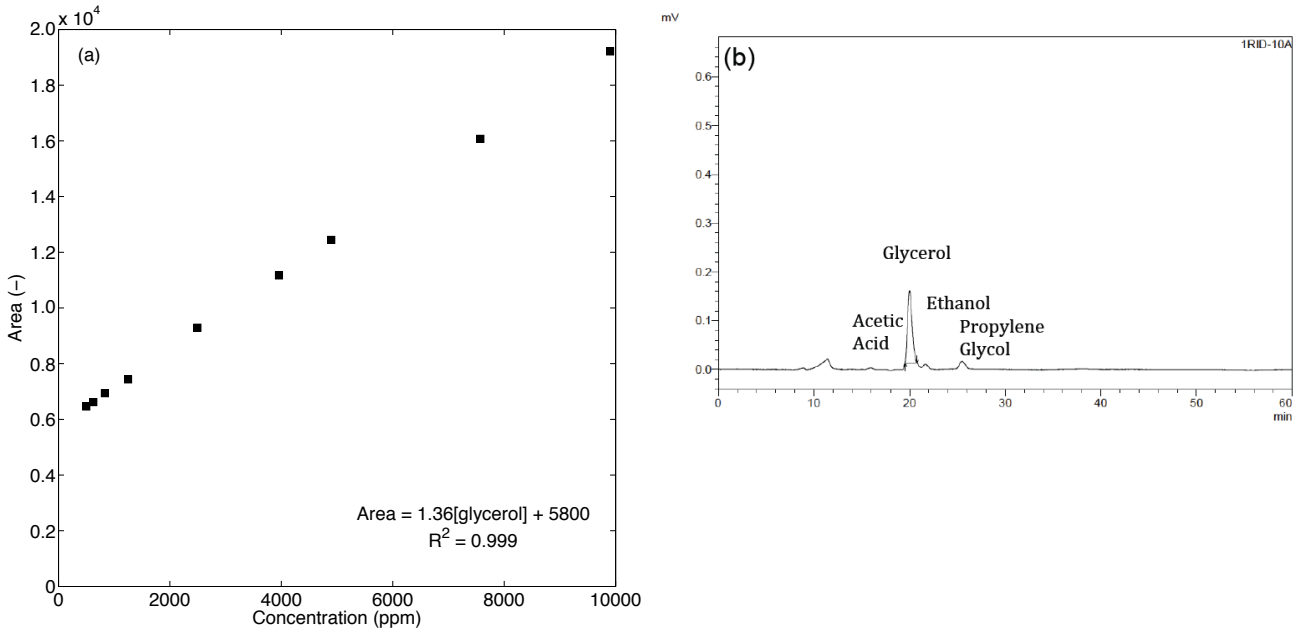


Figure S7. (a) HPLC calibration curve for glycerol; and (b) a representative HPLC analysis of the liquid product of APR over 1Pt-6Ni/3CeAl (240 ºC, 40 bar, 1 wt% glycerol, 0.05 mL min^{-1}, 250 mg catalyst).

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

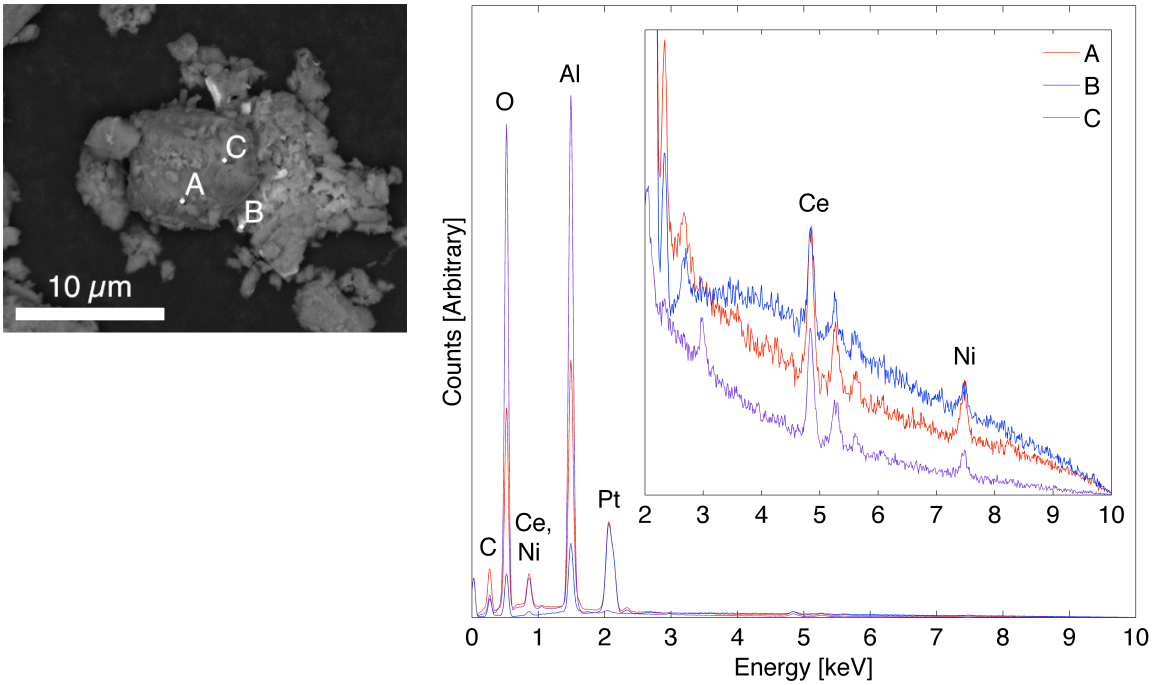


Figure S8. Energy-dispersive X-ray spectra of three spots on a 1Pt-18Ni/3CeAl catalyst that was reduced in flowing H_2 (50 vol% in N_2) at 800 °C for 60 min (heating rate 1.5 °C min^{-1}).

9. Ce 3*d* and Pt 4$d_{5/2}$ regions of the X-ray photoelectron spectra of fresh catalysts

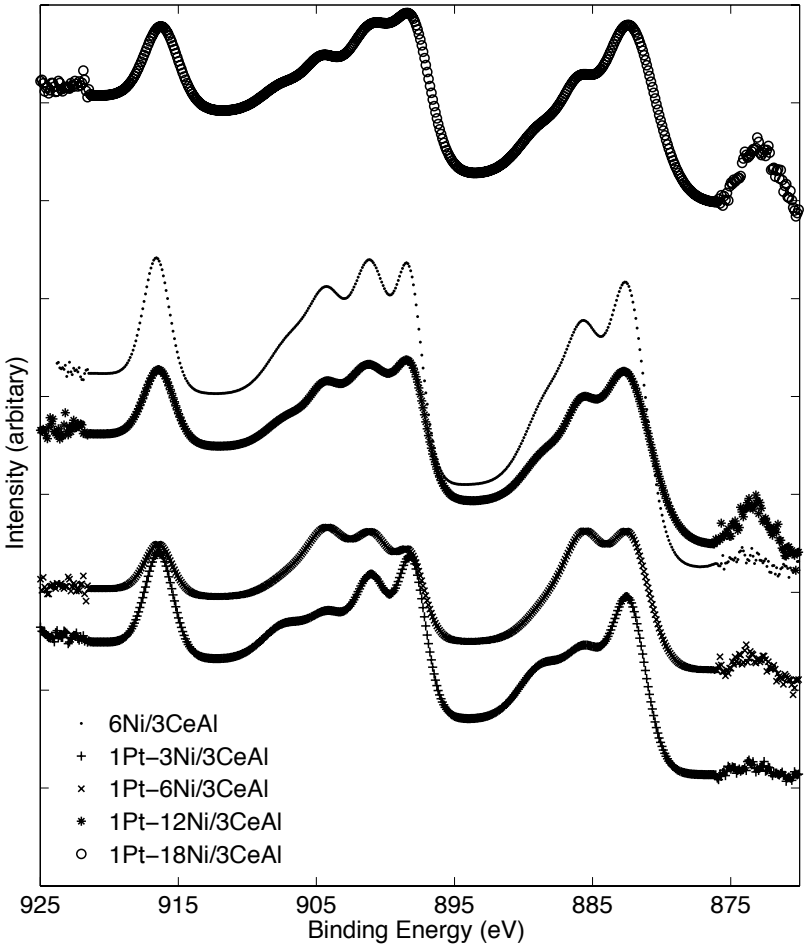


Figure S9 The Ce 3*d* region of the X-ray photoelectron spectra of xPt-yNi/3CeAl catalysts after reduction in flowing H_2 (50 vol.% in N_2) at 800 °C for 60 min (heating rate 1.5 °C min^{-1}).

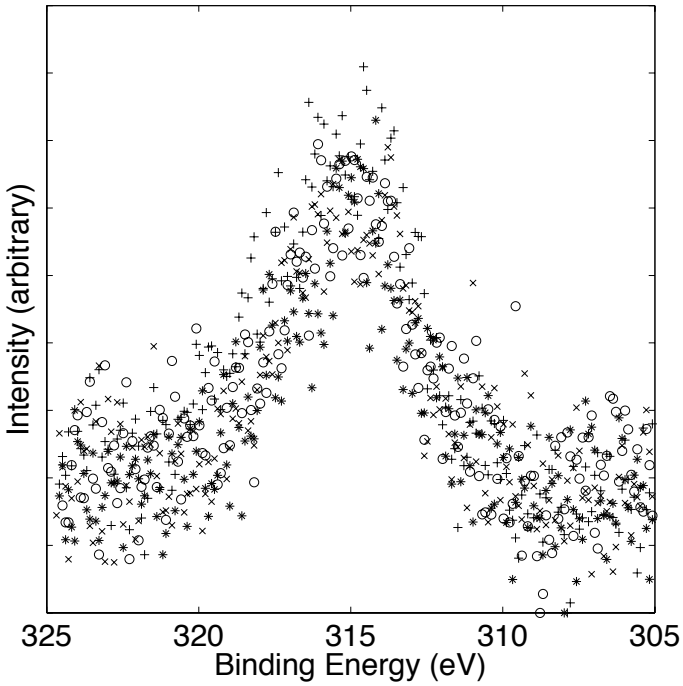


Figure S10. The Pt 4$d_{5/2}$ regions of the X-ray photoelectron spectra of 1Pt-yNi/3CeAl composites after reduction in flowing H_2 (50 vol.% in N_2) at 800 °C for 60 min (heating rate 1.5 °C min^{-1}). Baselines have been subtracted. No high-resolution spectrum of this region was obtained for sample 1Pt/3CeAl.

10. X-ray diffraction patterns of fresh and spent catalysts

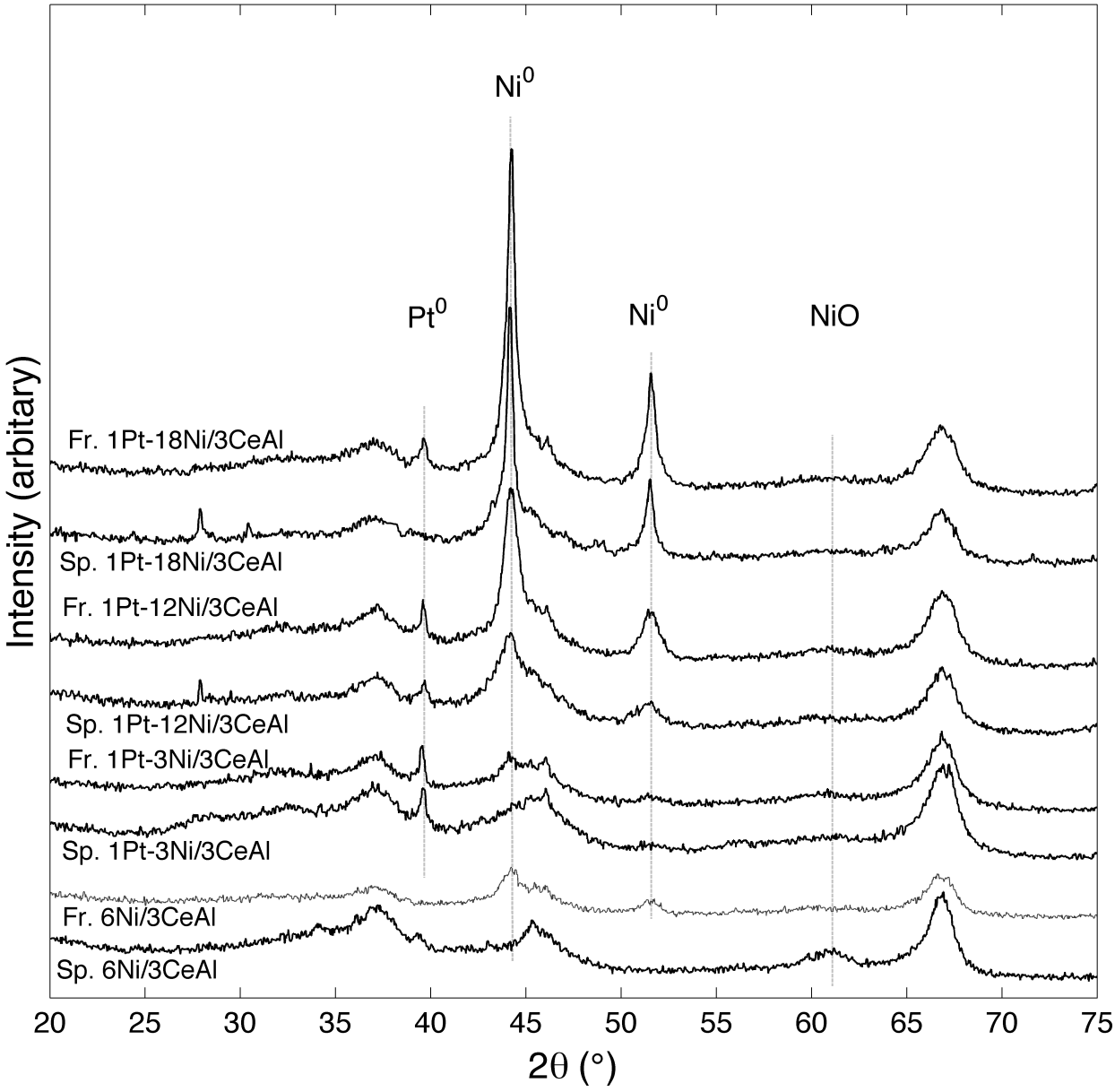
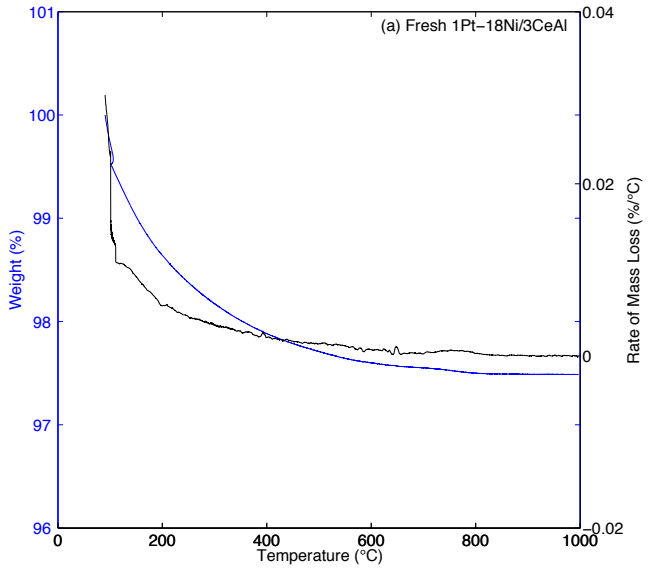
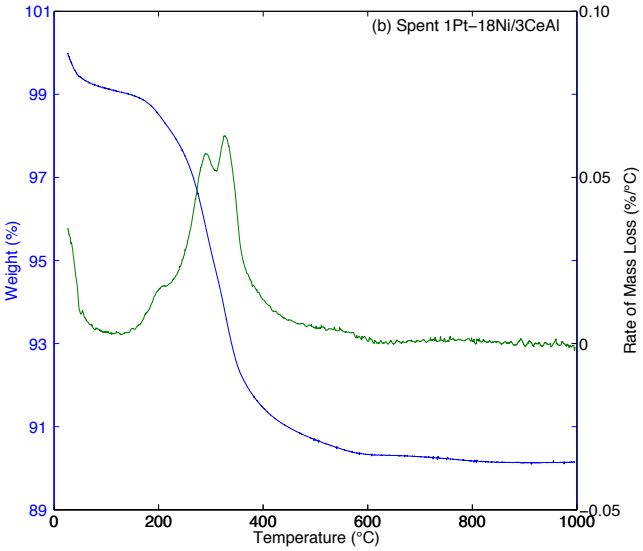
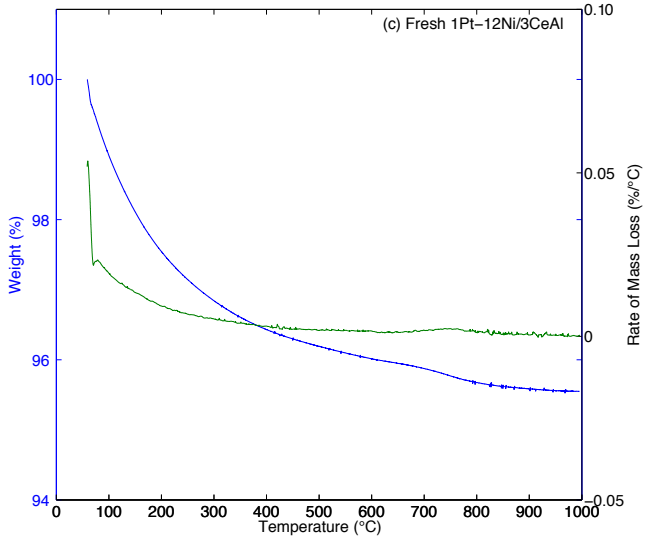


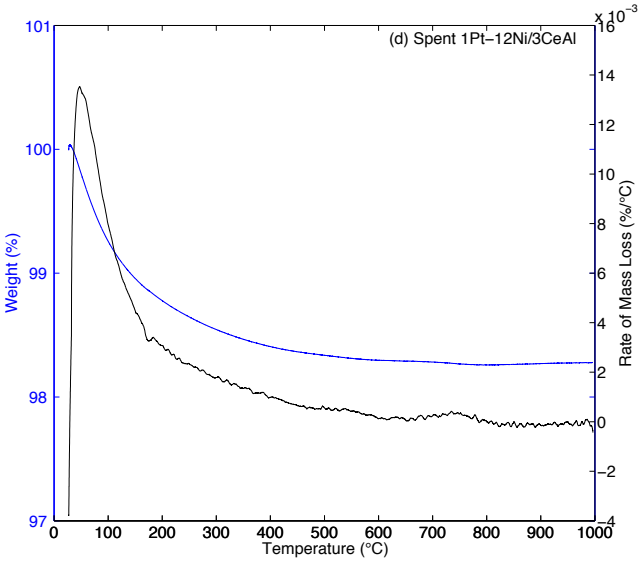
Figure S11. XRD patterns of catalysts freshly reduced in flowing H_2 (50 vol% in N_2) at 800 °C for 60 min, and of the spent catalysts after 30 h on stream in the APR of glycerol (240 °C, 40 bar, 1 wt% glycerol, 0.05 mL/min, 250 mg catalyst).

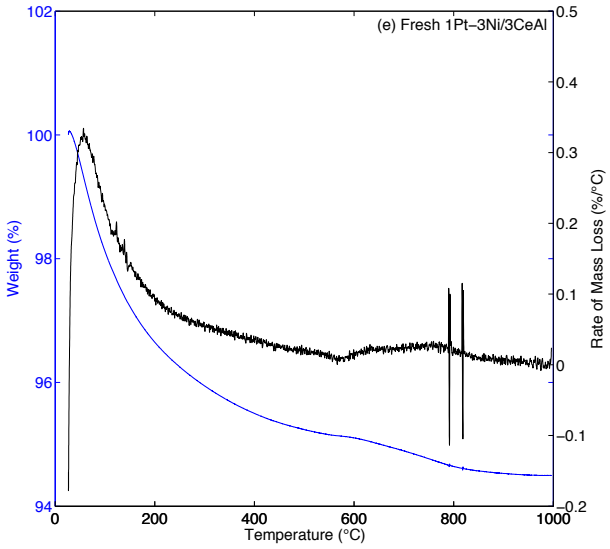
11. TGA curves

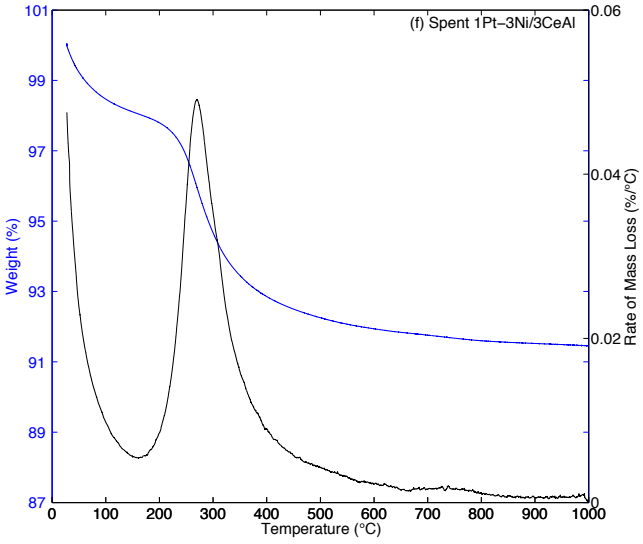












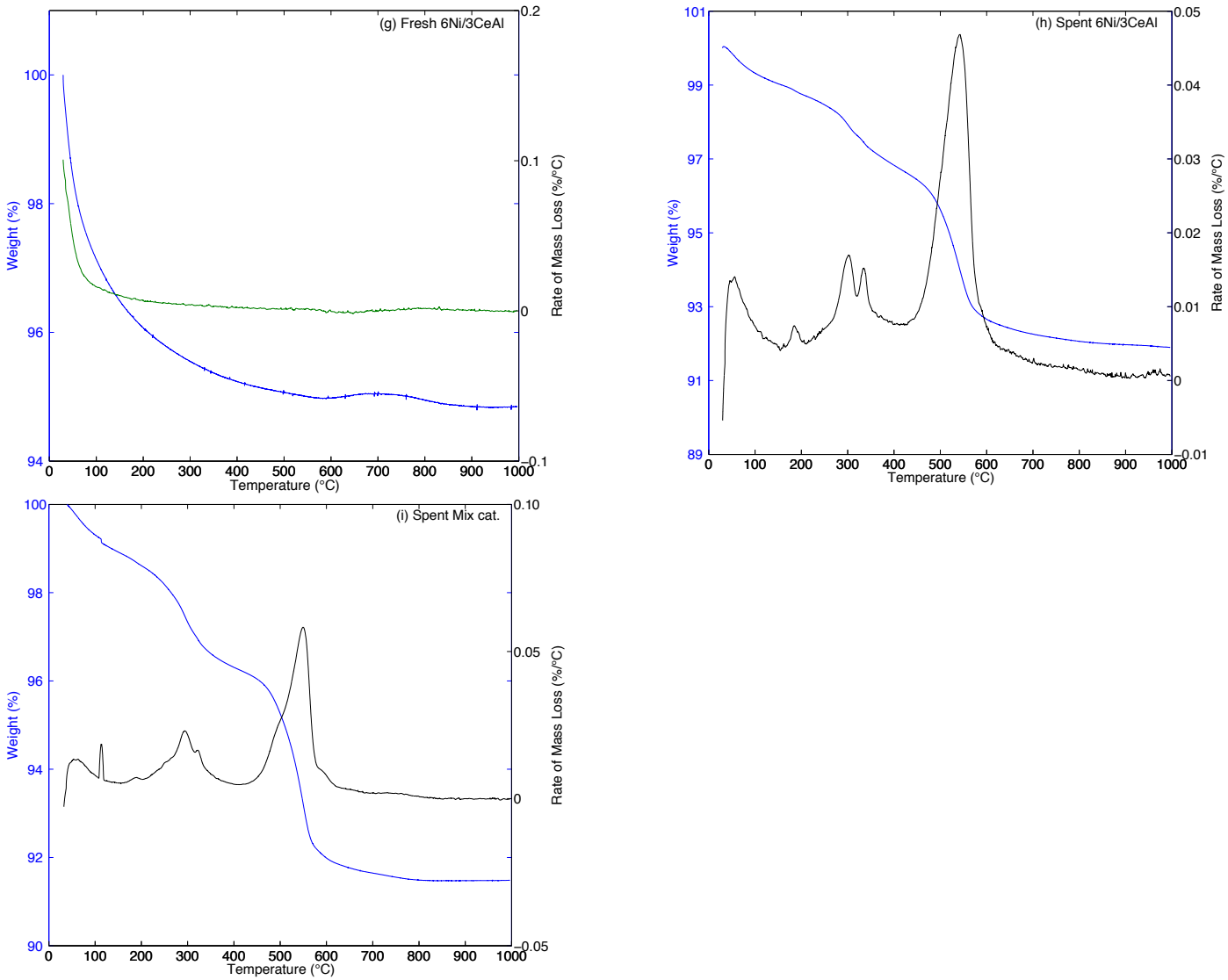


Figure S12. TGA analysis of (a) Fresh 1Pt-18Ni/3CeAl (b) Spent 1Pt-18Ni/3CeAl (c) Fresh 1Pt-12Ni/3CeAl (d) Spent1Pt-12Ni/3CeAl (e) Fresh 1Pt-3Ni/3CeAl (f) Spent 1Pt-3Ni/3CeAl (g) Fresh 6Ni/3CeAl (h) Spent 6Ni/3CeAl (i) Spent mixture of separate Pt/3CeAl and Ni/3CeAl catalysts with a total of 1 wt% Pt and 6 wt% Ni. In all cases, Fresh = catalysts freshly reduced in flowing H_2 (50 vol% in N_2) at 800 °C for 60 min, and Spent = spent catalyst after ≥30 h on stream in the APR of glycerol (240 ºC, 40 bar, 1 wt% glycerol, 0.05 mL min^{-1}, 250 mg catalyst). Samples were heated at 10 °C/min under instrument air (40mL/min).

12. X-ray photoelectron spectra of spent catalysts

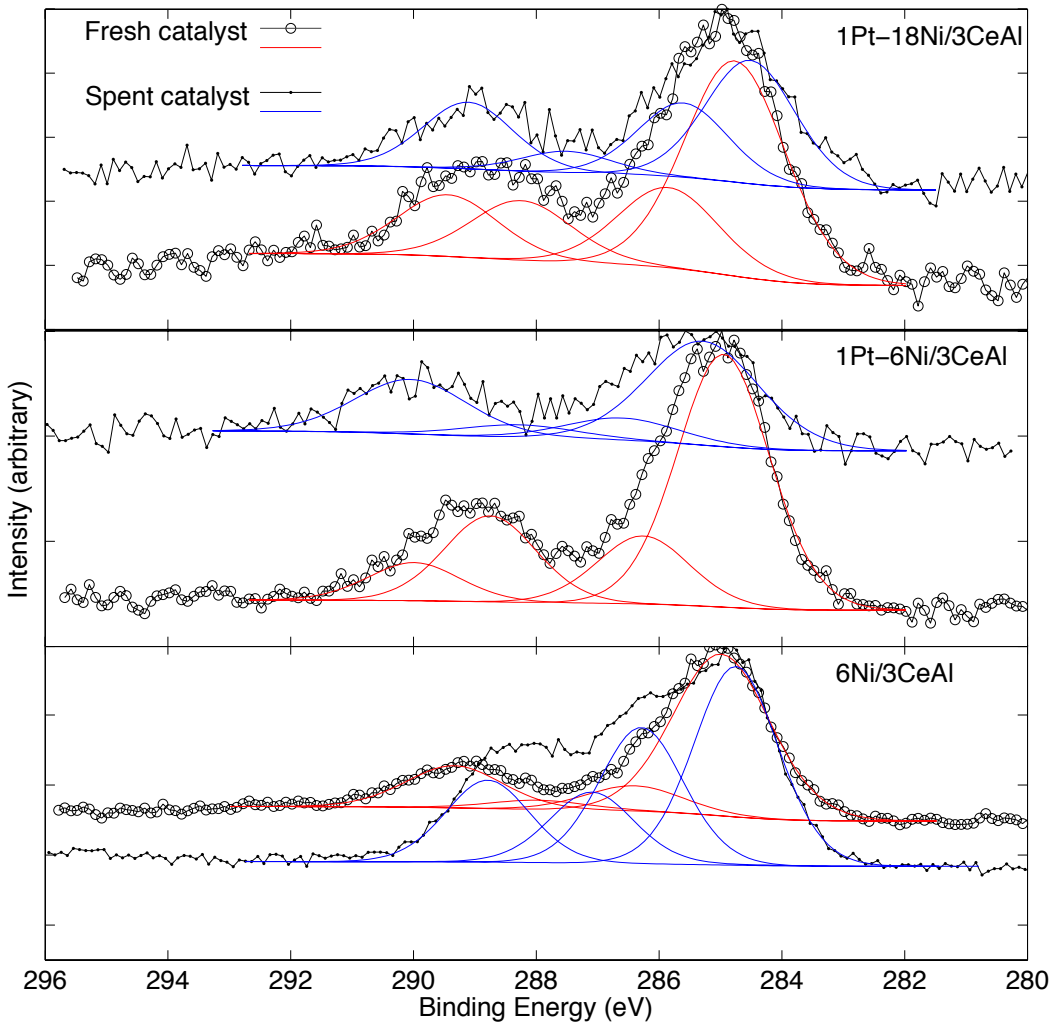


Figure S13 The C 1*s* region of the X-ray photoelectron spectra of xPt-yNi/3CeAl composites before and after use as catalysts in the aqueous phase reforming of glycerol for 30 h (6Ni/CeAl and 1Pt-18Ni/3CeAl) or 85 h (1Pt-6Ni/3CeAl). Traces for each sample were normalised to the intensity of the experimental 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.

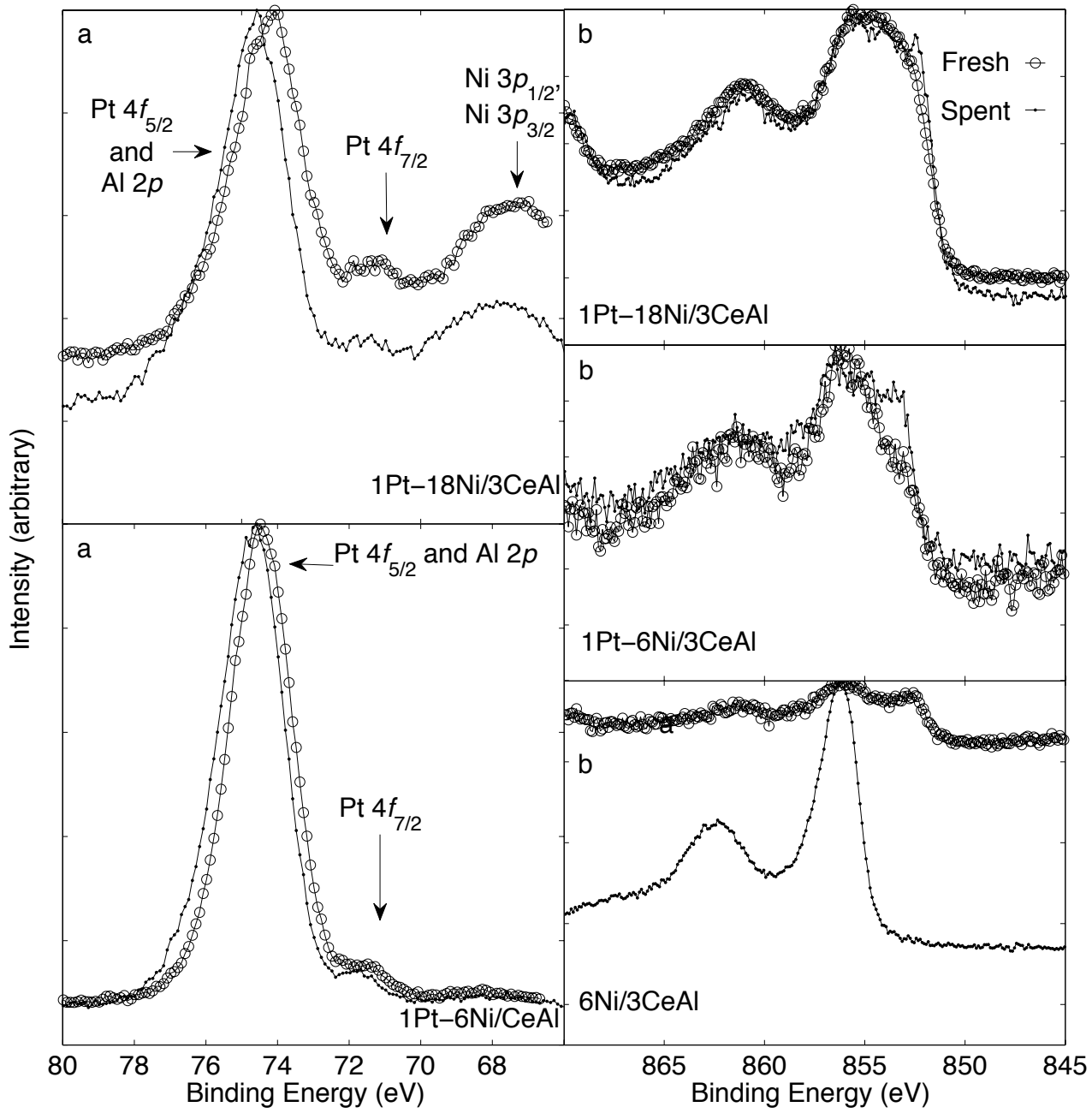


Figure S14. The (a) Al 2*p* and Pt 4*f* , and (b) Ni $2p_{3/2}$ regions of the X-ray photoelectron spectra of 1Pt-yNi/3CeAl composites before and after use as catalysts in the aqueous phase reforming of glycerol for 30 h (6Ni/CeAl and 1Pt-18Ni/3CeAl) or 85 h (1Pt-6Ni/3CeAl). Traces for each sample were normalised, so intensities cannot be compared among samples.