Supplementary material (ESI) for Journal of Materials Chemistry

Particle size – activity relationship for $CoFe_2O_4$ nanoparticle CO oxidation catalysts

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Supporting Information: Experimental, Figures S1-S10

Experimental

Coprecipitation route to samples C3-6 and C8-9

Sample C3 was prepared by dissolving 3 mmol of ethylenediamine (en) and 6 mmol of oxalic acid (ox) into 5 ml H_2O and heating in a solvothermal vessel of 23 ml capacity at 150 °C for 1 hour. Half of the resulting solution was added to 10 ml of a 0.1 M solution of $CoCl_2.6H_2O$ in H_2O at 70 °C and the other half to 10 ml of a 0.1 M solution of $FeCl_3.6H_2O$ in H_2O at 70 °C, with stirring. Approximately 3 ml of conc. HCl was added to each solution to remove the metal oxalate precipitates and the resulting pH was 1. They were then mixed together, and 3 M NaOH, also at 70 °C was added dropwise, with further stirring, to reach a pH of 12 whereupon the reaction was left for 1 hour. The solution was left to cool and then the liquid was decanted off, assisted by a Nd-Fe-B magnet of 28 mm diameter and 22 mm thickness. The black product was washed several times with H_2O and dried at 40 °C for 24 hours. The other samples were prepared following the same procedure however the compositions of the capping groups were different for each sample, as described in the main article.

Alternatively, the nanoparticles could be prepared more simply by following the procedure detailed in the main article, using the same amounts of reagents.

TEM images

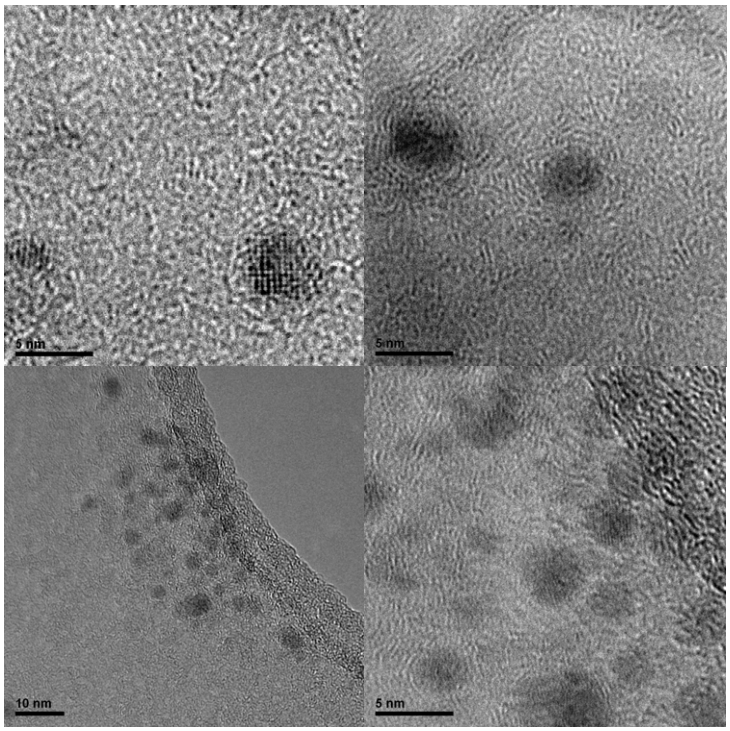

Figure S1 TEM images for sample C6, 5.8 nm ox-TEA capped nanoparticles.

N_2 Absorption Isotherms

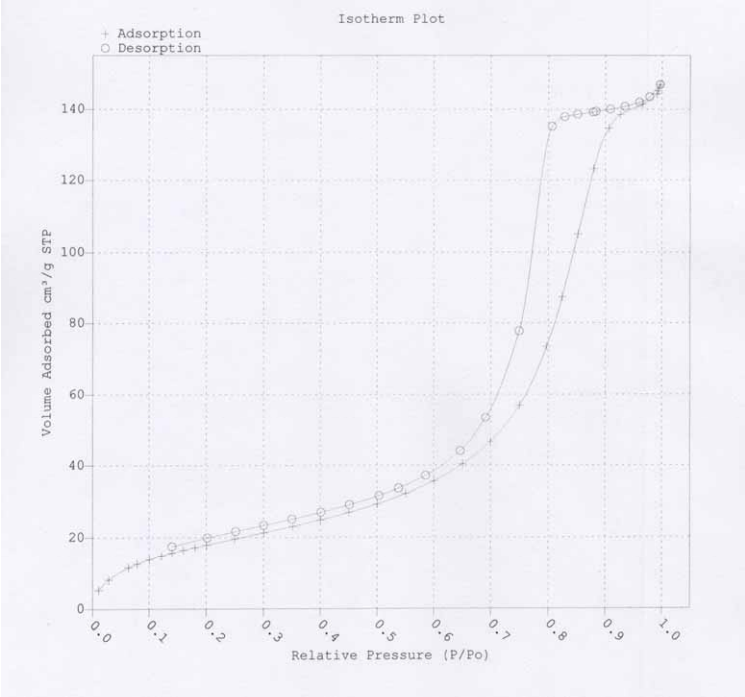

Figure S2 N_2 absorption and desorption isotherms for sample C2, 12 nm particles

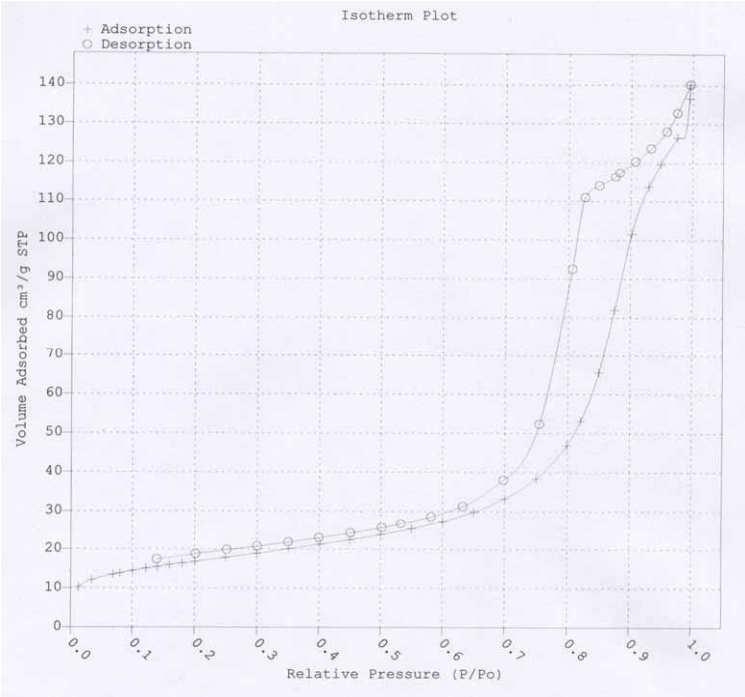

Figure S3 N_2 absorption and desorption isotherms for sample C10, 15 nm particles

The Type 4 character of the isotherms, together with pore-size distributions and particle sizes suggests that the particles are nonporous.

FTIR data

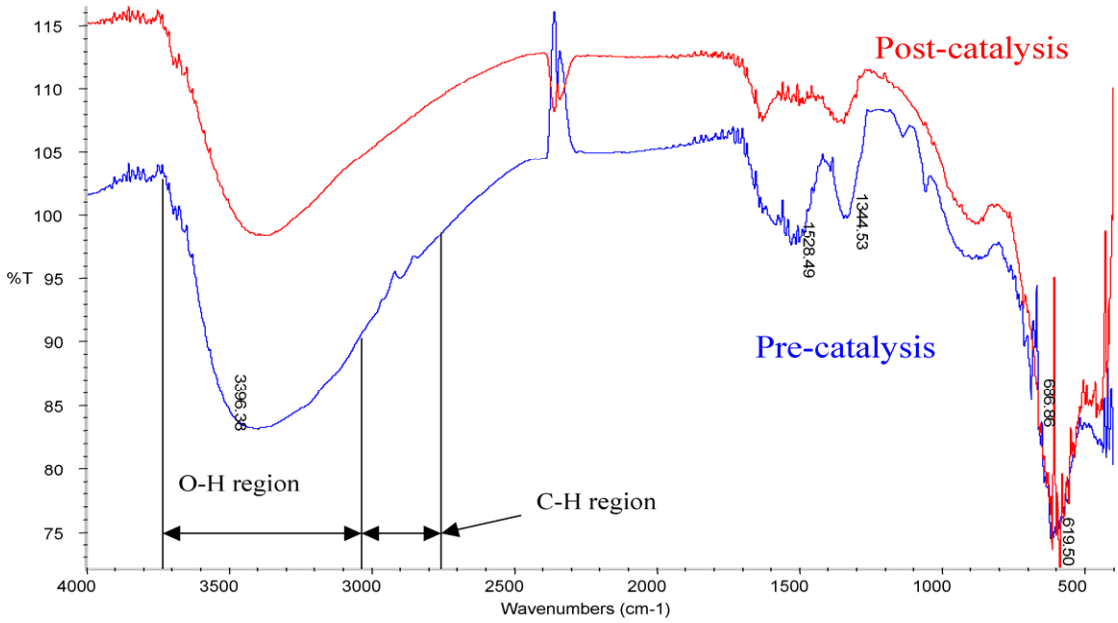

Figure S4 FTIR for sample C4, ox-en (1:1) capped $CoFeO_4$ nanoparticles

The strength of the O-H absorption band diminishes post-catalysis as the absorbed H_2O is removed. There is no strong C-H absorption. This is representative of the spectra for samples C3, C5 and C6. A 1% mixture of the samples in dried KBr was used for each of the spectra.

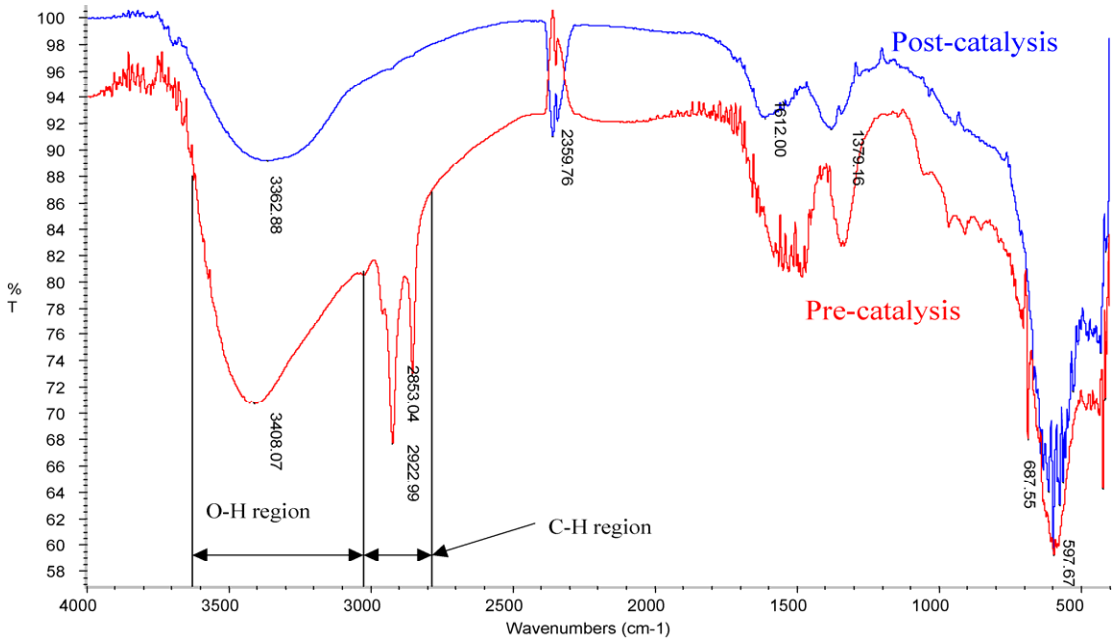

Figure S5 FTIR for sample C2, CTAB capped $CoFe_2O_4$ nanoparticles

Absorptions in the C-H region are present in addition to those in the O-H region. Both diminish post-catalysis.

TGA-MS data

TGA was carried out up to a temperature of 700 °C with a heating rate of 5 °C / min and a cooling rate of 10 °C / min under flow of N_2 at 20 ml / min.

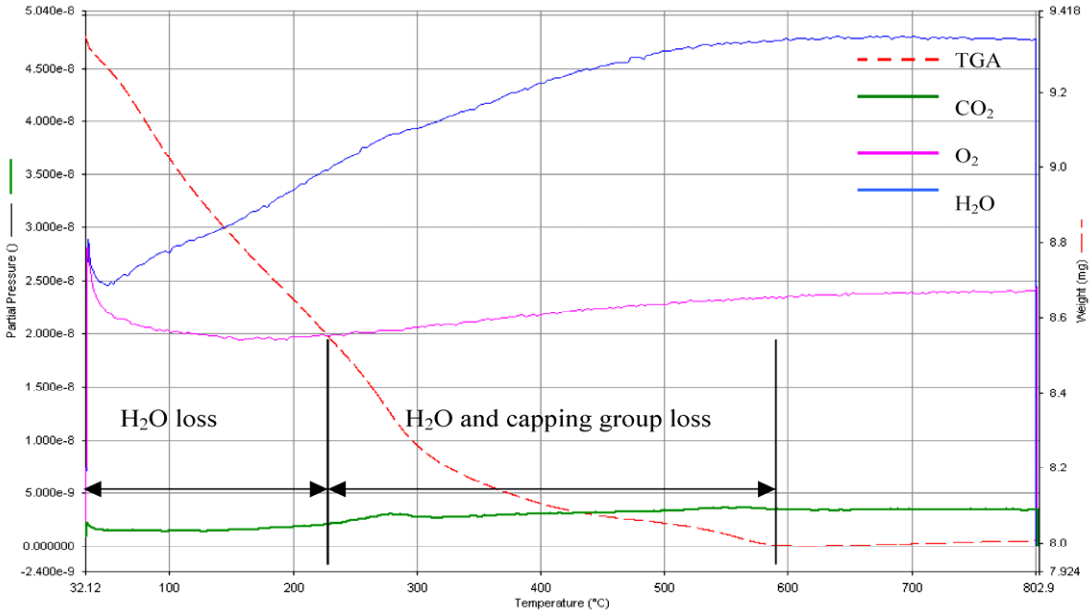

Figure S6 TGA-MS for sample C3, ox-en (2:1) capped nanoparticles. The above is representative of the TGA-MS for samples C4, C5 and C6

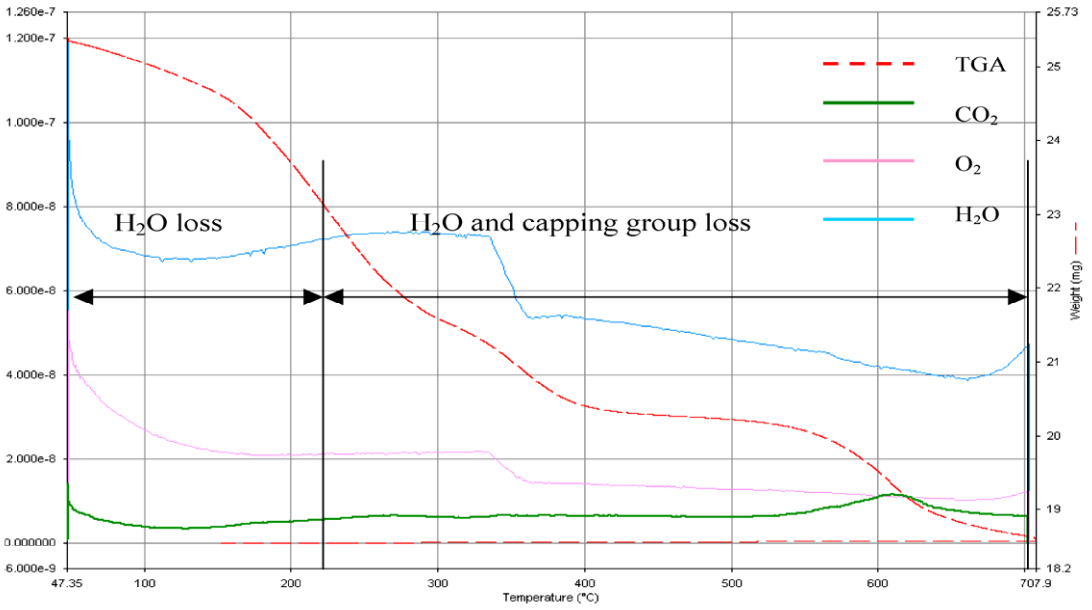

Figure S7 TGA-MS for sample C2, CTAB capped $CoFe_2O_4$ nanoparticles

Note: 220 °C is the point at which activation was observed during catalysis testing (for illustrative purposes, see Fig. 5 for this data for sample C1). The elemental analysis data taken from the post-catalysis sample C2 also shows a largely diminished carbon content, suggesting most of the capping groups were removed at this temperature.

Surface area data

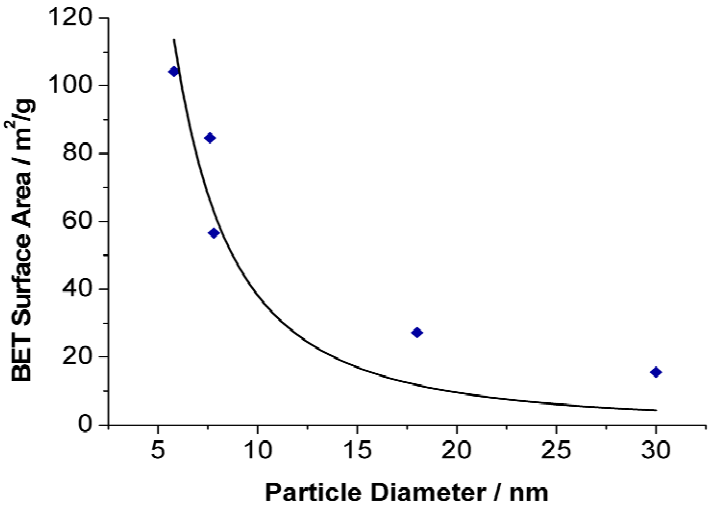

Figure S8 BET surface area versus particle size for samples C4, C5, C6 and C7. The data is fitted to the function $y = A\ x^{-2}$ where A is 3820 ± 377.

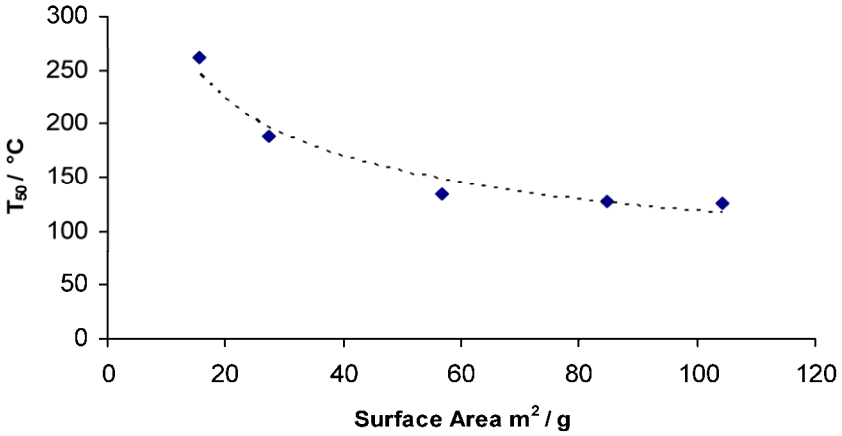

Figure S9 T_{50} versus BET surface area for samples C4, C5, C6 and C7. The line is a guide to the eye.

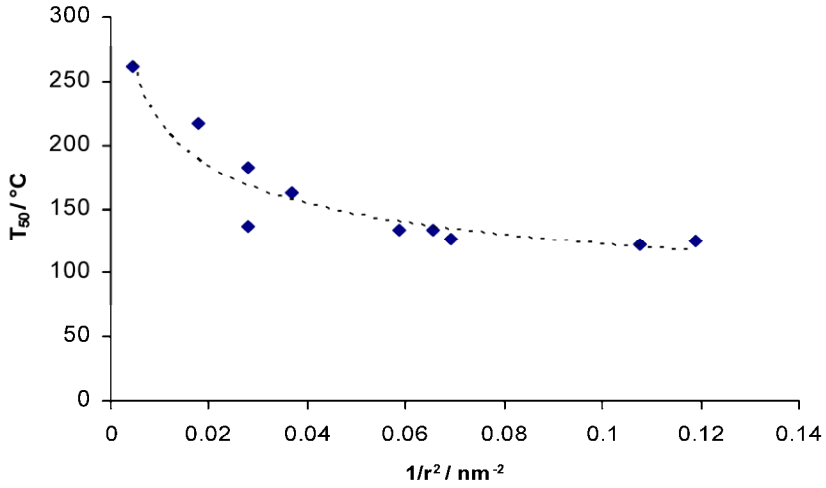

Figure S10 T_{50} versus $1/r^2$ for samples C1-10. The line is a guide to the eye.